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Laboratory scale modelling of soil vapour extraction (benzene, toluene, ethylbenzene, xylene).

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LABORATORY SCALE MODELLING OF SOIL VAPOUR EXTRACTION

By

Grant C. Hilbers

A Thesis Submitted to the
Faculty of Graduate Studies and Research
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ABSTRACT

An innovative in-situ remedial technology, soil vapour extraction (SVE), was simulated in the laboratory. Two types of soil, a sandy soil and an organic top soil, were packed into 1 m tall and 100 mm diameter stainless steel columns. Benzene, toluene, ethylbenzene and xylene, known collectively as BTEX, were added to the soils individually and as a mixture. Before addition to the soils, all contaminants were added to water, to achieve a concentration of 150 mg/L. The conditions simulated in this set-up were similar to those found in a gasoline contaminated soil that has undergone sufficient vapour stripping to remove the separate, non-aqueous, contaminate phase or a contaminant plume that has leached from a gasoline spill.

Three flow rates, 1.5, 3.0 and 6.0 L/h were used for each of nine sets of experiments. The four BTEX components were stripped individually and as a mixture, from sandy soil using dry air. Toluene was stripped, from sandy soil using moisture-saturated air also. In the final three experiments, the organic soil contaminated individually with, benzene, toluene and xylene was stripped. The initial moisture content in all these experiments was the field capacity of the soil. The rate of stripping was determined by analysing 1 mL aliquots of the exhaust air, from each of the columns, over the five day period that the experiments were conducted. Residual contaminant concentrations and distributions in the soil columns were determined at the end of each experiment and compared to the "Proposed Guidelines for the Clean-up of Contaminated Sites in Ontario".

The rate of stripping was observed to be greater when chemicals with higher vapour pressures were used. The mass fraction of benzene removed from the organic soil proved to be greater than the fraction removed from the sandy soil, at similar air flow rates. Both the use of saturated air for stripping and the stripping of toluene when present in soil as part of a mixture showed slower removal rates. The residual contaminant concentrations in parts of the soil columns were below the guideline levels indicating that SVE is a feasible remedial technology.

DEDICATION

Dedicated to my wife Jennifer for her continued support and encouragement.

ACKNOWLEDGEMENTS

I would like to thank my advisors Dr. J.K. Bewtra and Dr. N. Biswas for their guidance and support during this study. I would also like to thank Dr. B. Budkowska who offered a fresh perspective and continued encouragement throughout this project.

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1.0 INTRODUCTION

Air and water pollution are easily identifiable, sometimes even visible to the naked eye. The same cannot be said about soil pollution which is hidden and often neglected. Soil pollution usually impacts only a few people while air and water pollution can potentially effect large populations. Unlike air and water pollution, sites containing contaminated soils are finite in spatial extent which makes them unique in three ways. Land can often be traced to a single owner or a few owners, cleanup is economically possible and contamination poses a potential threat to surrounding properties and groundwater for long time.

Prior to the mid eighties, large sites contaminated with hazardous wastes were considered to be a priority and became the focus of most research and expenditure on soil remediation. This has changed over the last decade because it has been realised that of the various categories of soil contamination, such as hazardous leachate, agricultural waste and heavy metals, by far the largest number of active sites were contaminated with petroleum products (Sims, 1986). The most common source of petroleum contaminated soils are leaking underground storage tanks or LUSTs. In 1986, it was estimated by the EPA that 95% of an estimated 1.4 million regulated underground storage tanks in the United States were used to hold petroleum products (Sims, 1986).

Environment Canada estimates that 3-5% of the approximately 225,000 registered underground storage tanks in Canada are leaking. In Ontario, there are approximately 35,000 tanks at 12,000 sites. The Ontario Ministry of Consumer and Commercial Relations fuel safety branch predicts that approximately 10-15% of tanks installed prior to

1974 are leaking. In the United States, the EPA estimates that 10-30% of the approximately 5 million, registered and unregistered, tanks in the country leak (Delsan Environmental Group, 1994).

Gasoline, a common petroleum product, is a mixture of over 100 chemicals, most volatile and many partially soluble in water. Due to the mobility in the natural environment of many of the components of gasoline, there is often a high potential for groundwater contamination or vapour migration into surrounding structures.

In Ontario, contaminated soils must be cleaned up by land owners before the sale of properties or if contaminates have spread to the neighbouring properties. Clean up costs, which are paid by the land owner, average an estimated $50,000 US dollars (Delsan Environmental Group, 1994). One method of cleanup, commonly used in early remedial efforts, is to remove all contaminated soil and dispose of it in a secure landfill. This method is extremely costly and very disruptive to any operations which normally take place on the site. At one site in Indiana, the estimated cost of excavation and disposal was $520,000 while the cost of constructing and operating a soil vapour extraction (SVE) system was $50,000 (Dent *et al.*, 1990). Excavation is not a viable alternative at sites where contamination has spread across property lines or under structures. The total cost of cleanup must include the loss of use of the site, during the cleanup efforts, as well as direct cleanup costs.

Many alternative remedial methods have been developed, mostly based on trial and error approaches. Recently, more effort has been directed towards designing remediation programs based on sound scientific principles and data. Treatment of contaminated soil

off site, or ex-situ, has been largely replaced with in-situ treatment schemes. Typically, in-situ remediation is less expensive and less disruptive to activities conducted on a site.

One popular in-situ technology is soil vapour stripping or soil vapour extraction. The premise of this technique is to induce an air flow through contaminated soil for removing volatile contaminants. A practical limit on volatility of contaminants is 0.5 torr pure chemical vapour pressures or greater (Kearl *et al.*, 1991). One torr is equal to one mmHg at 0°C. At sites where contaminants are found deeper than 13 m (40 ft), SVE is one of the only feasible remedial methods (Malot and Wood, 1985). Gasoline contaminated soils are suitable for this type of remediation due the high volatility of the majority of the components that constitute gasoline.

The composition of gasoline is not universal, but most components are present within a practical range. Though there are many chemicals present in gasoline, four in particular are of concern with regard to water pollution and adverse health effects. These chemicals are benzene, ethylbenzene, toluene and xylene, commonly referred to as BETX (pronounced Bee-Tex). The chemical of most concern is benzene, which is a proven human carcinogen.

Table 1 contains some pertinent information regarding BETX contaminated soils. Site occurrence and average concentration are based on data collected by the EPA (Lyman et. al., 1992).

The soil vapour extraction method has been used successfully at various sites across North America, but most implementations to date have been based on empirical data. Often the chemical and physical interactions taking place are not well defined. In

addition, relatively few case studies are available on which to base a feasibility study to determine its effectiveness at potential remedial sites. Computer modelling has become a common design tool and is typically more accurate than empirical designs, especially for large sites (Fam *et al.*, 1996).

Table 1 - Typical Site Occurrence of BTEX

CONTAMINANT	VAPOUR PRESSURE (mmHg @ 12 °C)	AVERAGE SITE OCCURRENCE (%)	AVERAGE CONCENTRATION (mg / kg)
Benzene	59.3	28.5	1.6×10^4
Ethylbenzene	4.37	26.9	5.4×10^5
Toluene	14.0	44.1	1.1×10^6
Xylene	2.96	9.8	6.9×10^5

In order to fully understand soil vapour stripping, a wide range of soils and chemicals would have to be studied. Among the properties expected to effect the rate of contaminant movement are: permeability, moisture content, grain size distribution, organic content and temperature of the soil. The solubility, vapour pressure and density of the chemicals would also be important parameters (Rathfelder *et al.*, 1991). Current models are based on a large number of unproved assumptions.

1.1 Objectives

The first objective of this study was to determine the relationship between the rate of stripping of selected chemicals and soil properties under different air flow rates. The second objective was to determine the residual chemical and moisture distributions in soils

that have been stripped of contaminants and compare the results to legislated clean-up criteria.

1.2 Scope

The scope of this project was limited to laboratory scale experiments. A total of 27 soil column experiments were conducted. Two different soils were used: a sandy soil and a soil with high organic content. The sandy soil was used because it was inert and relatively uniform. The organic soil was used to determine the effect of chemical adsorption on soil vapour extraction. These two soil were used because they were uniform and well defined.

All four BTEX components were added separately to individual soil columns in solutions of approximately 150 mg/L. Dry air was used at three different flow rates during the stripping experiments. A combination of all four BTEX components was stripped from sandy soil at three different air flow rates. Finally toluene was stripped from a sandy soil using saturated air.

The concentration of the air stream leaving each column was recorded over a five day period to determine the rate of stripping. At the end of each experiment, samples were taken at different depths from each column and analysed to determine the residual chemical concentration and the final moisture distribution.

2.0 SOIL VAPOUR EXTRACTION PROCESS OVERVIEW

Soil Vapour Extraction or Soil Vacuum Extraction (SVE) is a remedial technique that involves inducing an air flow through contaminated soil in the unsaturated or vadose zone. The vadose zone in a soil is defined as the region between the ground surface and the water table. To generate a flow, air is introduced into injection wells and removed through extraction wells. The pressure in the injection wells must be higher than the pressure in the extraction wells.

There are two basic approaches to the design of SVE systems: either a blower is used to force air into the injection wells or a vacuum pump is used to reduce the pressure in the extraction wells. In both cases, an air pollution control (APC) device is normally required to remove contaminants from the extracted air. A typical APC device is a biofilter which not only removes contaminants from the air stream but, if designed correctly, uses bacteria to degrade the contaminants and there by eliminating the hazard completely. A simple vapour extraction system is illustrated in Figure 1.

Vapour extraction is economical only in the unsaturated zone because the water table forms an impermeable barrier to air flow. Contaminants that have migrated into the groundwater can be removed to some degree as the soil above is cleaned and a concentration gradient develops. Often spilled chemicals, such as gasoline, are lighter than water and will float on the ground water table. These contaminant lenses can be effectively removed using SVE.

Contaminants that are not miscible in water are classified as non-aqueous phase liquids (NAPLs). When the specific gravity of a contaminant plume is less than 1, it is

further classified as a light NAPL (LNAPL). Dense NAPLs (DNAPLs) are heavier than water and will sink to low points of aquifers into which they are spilled. A common DNAPL, found at many contaminated sites, is Tricloroethylene (TCE). These compounds are not suitable for removal by using the SVE method.

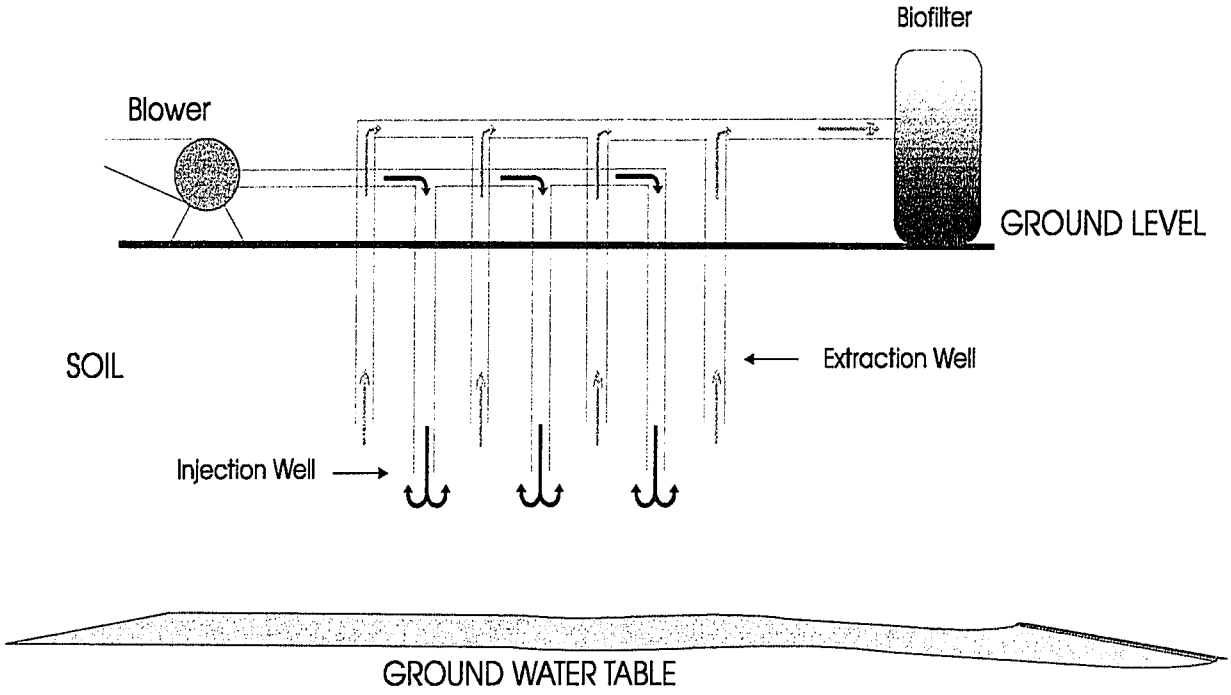


Figure 1 - Vapour Extraction System

As gasoline, a LNAPL, travels through the unsaturated zone a trail of droplets is left behind. Drops of pure chemical are also spread, from free floating product, when the ground water table rises and falls through natural fluctuations. This area, typically between the high and low water level, is known as the smear zone.

In addition to pure chemical, there are several other phases in which contaminants can be found. Partitioning will occur between the pure chemicals and the air and water held in the pore spaces between particles. In addition, some contaminants will be

adsorbed to organic matter as well as onto mineral surfaces. Contaminants in the liquid phase are possibly present in the ground water, in the liquid film coating particles and in liquid absorbed by solid particles. If both pure chemical and water are in contact with solid particles, the pure chemical will float on the water surrounding the particle as seen in Figure 2.

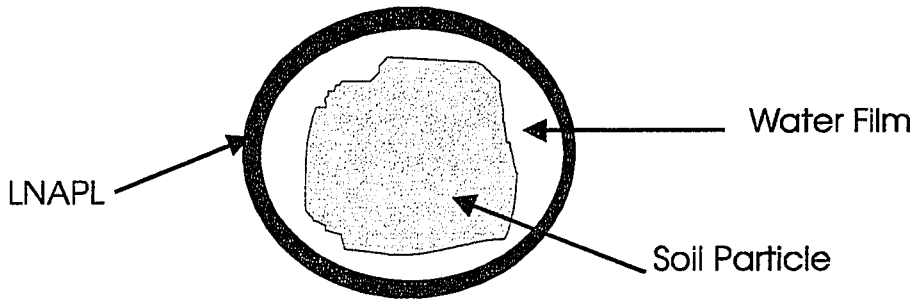


Figure 2 - LNAPL Distribution on a Pore Scale

At an undisturbed site, the contaminants in the various phases will nearly be in equilibrium which is dependent a variety of chemical and soil properties. The air flow induced during soil venting will reduce the concentrations in the gas phase below the equilibrium concentration, causing contaminants to diffuse into the gas phase. For SVE to be considered economical, sufficient fluxes must be induced between the pore gas and all other phases. There are two conditions that must be met to consider SVE a viable alternative. Firstly, the soil in the unsaturated zone must be permeable enough to allow sufficient gas flow and secondly the contaminants being removed must be reasonably volatile.

The rate of volatilisation is directly dependent on the pure chemical vapour pressures of the contaminants which are in turn a function of temperature. Increases in the vapour pressure and temperature increase the rate of volatilisation. Soil moisture content

is also an important factor that effects removal efficiency in two ways. Higher moisture content reduces air space in voids which in turn reduces volatilisation. Also, as moisture increases, electrostatic forces in the soil decrease which leads to an increase in volatilisation. Taking both of these factors into account, there exists an optimal moisture content at which stripping is most effective (Lyman *et al.*, 1992).

2.1 Design Factors

The design and installation of a SVE system is relatively simple but to optimise a system, detailed knowledge of the soil parameters that effect this process is essential. Many designers overlook the theory governing the operation of a SVE system (Fam *et al.*, 1996).

Before a remediation system can be implemented, an intensive hydrogeological investigation must be conducted. Both the extent of contamination and the subsurface conditions are identified through this investigation.

2.1.1 Site Preparation

To enhance the effectiveness of SVE, the groundwater table can be lowered during the initial construction to increase the volume of the unsaturated zone. In addition to this, an impermeable cap is often placed above remedial sites. This reduces the infiltration of water and prevents the subsurface air flow from short-circuiting. Short-circuiting will cause areas farthest from the wells to receive inadequate air flow, greatly increasing clean-up time. To minimise this wells should not be screened within 1.5 m (5 ft) of the ground surface (Sims *et al.*, 1996).

Well distribution is determined by soil heterogeneity and site topography. It is difficult to effectively design wells in stratified soils because air flow will preferentially flow through the layers of soil that are more permeable.

2.1.2 Chemical Properties

The properties of the chemical being removed from the soil are important in determining the distribution of contaminants within the subsurface and their rate of removal. The key properties of interest are the vapour pressure, Henry's law constant and solubility.

At most remedial sites the soil is relatively moist with a moisture content around 10% by mass (Fam *et al.*, 1996). Under this condition, most contaminants dissolve into the pore water. The solubility of a chemical determines the maximum concentration in the pore water. Microbial degradation of contaminants is also enhanced when contaminants are dissolved in water. During vapour extraction along with the chemical removal, pore water is oxygenated enhancing degradation of certain contaminants. If this is the primary means of remediation, the method is termed 'Bioventing'.

If a NAPL is present in the soil matrix, then the pure chemical vapour pressure is important. This determines the equilibrium concentration between the NAPL and the pore air. Compounds with high vapour pressure are more effectively removed using SVE. Chemicals with low vapour pressures are removed slowly and are often more successfully removed through bioventing.

The adsorption of contaminants onto organic and mineral surfaces can reduce the effectiveness of SVE. The extent of adsorption is dependent on chemical properties, soil organic content and the moisture content.

The molecular mass, size, elecronegativity and polarity of compounds affect extraction and bioventing. Large molecules tend to adsorb to soils more readily. The age of a spill also affects the rate of SVE because the longer a mixture, such as gasoline, sits the more dispersion of mobile components will occur, leaving behind the more difficult components to remove. An old spill is typically referred to as a 'weathered' spill.

2.1.3 Soil Moisture

For each soil-contaminant combination, there exists an ideal moisture content. Both higher and lower moisture contents will adversely affect SVE. When the soil moisture content is high, advection is limited because air will flow through fewer pathways. Volatile organics typically travel 10,000 times faster through air than they do through water (Fam *et al.*, 1996). Thus it would seem that drier soils would be ideal, however, at lower moisture contents mineral surface adsorption becomes predominant. At moisture contents below 2%, adsorption to mineral surfaces controls the rate of mass transfer. This leads to slow, non-equilibrium vapour stripping. The critical moisture content, when decrease in SVE becomes apparent, is typically defined as one monolayer of molecules coating the soil surfaces. This occurs at 2 to 4% moisture in a soil. At moisture contents above 4%, adsorption to organic matter is dependent on chemical properties. When soil surfaces are covered with five layers of water, Henry's law will become dominant over mineral adsorption (Sami *et al.*).

Drying a soil permanently affects the desorption capacity of a soil, causing adsorption-desorption hysteresis. Soil venting may become ineffectual when the soil moisture becomes so low that the contaminants become bound to soil surfaces.

2.1.4 Soil Properties

Along with moisture and organic content, a soils porosity is an important characteristic. The range of values for porosity for four particle size categories are presented in Table 2 (Freeze and Cherry, 1979).

Table 2 - Range of Values of Porosity for Soils

DESCRIPTION	POROSITY %
Gravel	25-40
Sand	25-50
Silt	35-50
Clay	40-70

Soils with low porosity generally are less effectively vented because diffusive transport through the soil matrix is limited (Sami *et al.*, 1996). Typically, granular soils with low porosity also have higher surface area providing more sites for surface binding. Clays do not follow this trend. The relationship between particle diameter and surface area can be seen in Table 3 (Hillel, 1980). A combination of porosity and moisture content determine the air permeability of a soil. Soils with low permeability will not receive a high air flow rate, thus limiting the mass transfer of contaminants into the air.

Table 3 - Relationship Between Particle Diameter and Surface Area

Diameter of Particles (mm)	Description	Approximate Surface Area (m^2/g)
1.0-2.0	Very Course Sand	0.001-0.003
0.5-1.0	Coarse Sand	0.003-0.005
0.25-0.5	Medium Sand	0.005-0.01
0.1-0.25	Fine Sand	0.1-0.03
0.05-0.1	Very Fine Sand	0.03-0.1
0.002-0.05	Silt	0.1-1
<0.002	Clay	> 1
<0.002	Activated Clay	1.50-2.25

Organic soils can be harder to clean because the adsorption of contaminants can occur. The rate of removal of VOCs from a highly organic soil is difficult to determine due to hysterisis. This phenomenon tends to slow vapour extraction because the energy required to adsorb the chemicals is less than that required for desorption.

3.0 LITERATURE REVIEW

An extensive literature review was conducted focusing on pertinent articles pertaining to the properties of the chemicals used in this study (BTEX), the current legislation in Ontario regarding the cleanup of contaminated sites and the field and laboratory findings on SVE methods.

Soil vapour extraction has been applied to many sites across North American and a fair amount of data has been complied regarding the types and concentrations of contaminants found. Researchers should avail themselves to these data to ensure that laboratory work reflects real world conditions.

3.1 Chemical Properties

The characteristics of the contaminants in a soil being remediated are important to the design of a successful clean-up scheme. The impacts on both human and environmental health are considered by legislators when determining clean-up criteria or goals. It is also important for a designer to be aware of the potential health impact of the chemicals being remediated in order to avoid exposing workers or the public to unsafe conditions while a clean-up is underway.

The physical characteristics of contaminants must be considered when planning a viable remedial plan. When specifically dealing with SVE, the properties of most interest to a designer are the pure chemical vapour pressure, Henry's law coefficient and possibly the Octanol water coefficient (Koc) - which quantifies a chemicals adsorption potential onto the organic matter. Henry's law coefficient quantifies the equilibrium concentration

partitioning between water and air. It is unique for each chemical and is a strong function of temperature.

The experiments that were conducted during this study were conducted using some of the most significant components of gasoline - BTEX. The structure of all four components, which are classified as aromatic hydrocarbons, can be seen in Figure 3. Benzene is the chemical of most concern because it is a proven human carcinogen and relatively mobile in the subsurface environment.

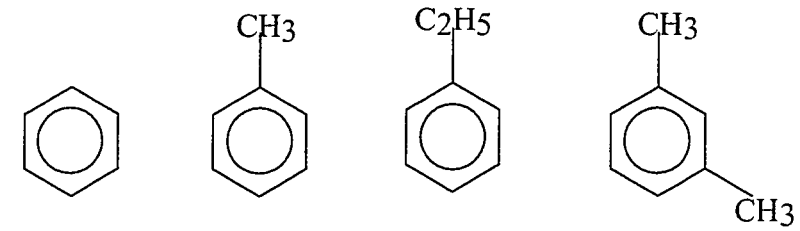


Figure 3 - The Chemical Structures of BTEX

3.1.1 Health Effects

The health effects of the BTEX components, presented below, were adapted from Lewis (1991). More detailed information is widely available in the literature.

3.1.1.1 Benzene

Benzene is a confirmed human carcinogen producing myeloid leukemia, Hodgkin's disease, and lymphomas by inhalation. In pure form it is a clear, colourless liquid. It is a human poison by inhalation and moderately toxic by ingestion and by introduction through cuts and abrasions. Human effects include euphoria, somnolence, changes in REM sleep, changes in motor activity, nausea or vomiting, reduced number of blood platelets,

dermatitis and fever. Acute exposure is usually non-fatal and recovery is normally complete. Chronic exposure is more dangerous as benzene has a cumulative effect.

3.1.1.2 Toluene

Toluene is a colourless liquid with an odour similar to benzene. It is only moderately toxic by intravenous, subcutaneous and possibly other routes. When inhaled it is mildly toxic and has been shown to cause human systemic effects. These effects include hallucinations, motor activity changes and bone marrow changes. Experimental teratogenic (causing mutations to foetuses) and reproductive effects have been shown. Toluene is a flammable liquid and a fire hazard.

3.1.1.3 Ethylbenzene

It is a clear colourless liquid with an aromatic odour, moderately toxic by ingestion and intraperitoneal route and mildly toxic by inhalation and skin contact. Human effects by inhalation include eye, sleep and pulmonary changes. A concentration of 0.1% in air has been found to be an eye irritant and 0.2% concentration becomes a sever irritant. Exposure of Guinea pigs to 1% concentration has been reported to cause ataxia, loss of consciousness, tremors in the extremities and finally death due to respiratory failure. Ethylbenzene is a very dangerous fire and explosion hazard.

3.1.1.4 Xylene

Xylene is moderately toxic by intraperitoneal (injection directly into abdominal cavity) and subcutaneous (injection below the skin surface) routes and mildly toxic through ingestion and inhalation. Human systemic effects through inhalation include:

olfactory changes, conjunctiva irritation and pulmonary changes. Experimentally, xylene has been shown to have reproductive and teratogenic effects. It is a very dangerous fire hazard when exposed to heat, flames or oxidising agents.

3.1.2 Physical Chemical Characteristics

There are a number of compilations available that list the chemical properties of the constituents of gasoline. The values compiled in Table 4 were adapted from Heath *et al.* (1993). A summary of properties of a synthetic gasoline developed for laboratory use, containing 23 representative compounds, was presented by Lyman *et al.* (1992). Wilson and Clark (1994) have provided extensive data on the vapour pressure and Henry's law constant for a wide variety of contaminants across a large temperature range. The surface water half-life is an estimate of the time, in days, needed for the mass of a contaminant spilled on surface water to be reduced by half.

The composition of gasoline is not uniform but individual components are typically present within a practical range. Table 5 contains information on the expected concentrations of BTEX found in unleaded gasoline, and the corresponding concentrations that would be found in water in equilibrium with a pure gasoline phase (Heath et al., 1993).

3.1.3 Site Occurrence

Several collections of case studies, containing detailed site information, have been published. One excellent article, covering 17 different sites, was written by Hutzler *et al.* (1989) who conducted much of the important early work on SVE.

Table 4 - Characteristics of BTEX

COMPONENT	Molecular Mass (g / mol)	Water Solubility (mg/L @ 25 °C)	Specific Gravity	Vapour Pressure (mmHg 25°C)
Benzene	78	1780	0.88	95
Toluene	92	490-627	0.87	28
Ethylbenzene	106	152-208	0.87	9.5
m-Xylene	106	173	0.87	10

COMPONENT	Henry's Law Constant (atm-m^3 / mol 25°C)	Diffusivity (mm^2 / s)	Koc (mL / g)	Surface Water Half-Life (days)
Benzene	5.5E-03	9.30	49-100	5
Toluene	6.7E-03	7.80	115-150	4
Ethylbenzene	8.7E-03	6.70	95-260	3
m-Xylene	6.3E-03	7.20	1585	7

Table 5 - Composition of Gasoline - BTEX components

GASOLINE COMPONENT	REGULAR UNLEADED GASOLINE MASS (% by mass)	REGULAR UNLEADED GASOLINE VOLUME (% by volume)	WATER-SOLUBLE-PHASE REGULAR UNLEADED GASOLINE (µg / L)
Benzene	0.12-3.5	2-5	30,500
Toluene	2.73-21.8	6-7	31,400
Ethylbenzene	0.36-2.86	5	4,040
Xylenes	1.77-3.87	6-7	13,900

3.2 Legislation

The decision to remediate a property is normally in response to legislation. Legislated guidelines are normally set at the provincial or state level. In the United States, in 1991, the cleanup criteria ranged from 1 to 500 ppm_{mass} total petroleum hydrocarbons (TPH) in various states (Pedersen and Curtis) .

The discussion presented below focuses on legislation in Ontario. The bulk of the information presented here is based on the "Proposed Guidelines for the Clean-up of Contaminated Sites in Ontario", published in July, 1994, by the Ministry of Environment and Energy. The authority for the MOEE to order site remediation is found in the Environmental Protection Act (1990).

3.2.1 Assessment and Clean-up

The requirements to remediate a specific site vary considerably and should be fully documented and retained by the property owner. The generic approach to assessment and clean-up, shown in Figure 4, can be used as a template.

3.2.2 Clean-up Criteria for BTEX in Ontario

Tables 6-10 contain cleanup criteria for BTEX applicable to all possible site use classifications that are allowed under the MOEE guidelines. The values given represent the maximum allowed concentrations for each contaminant. The background levels shown in Table 8 are only used for properties classified as environmentally sensitive.

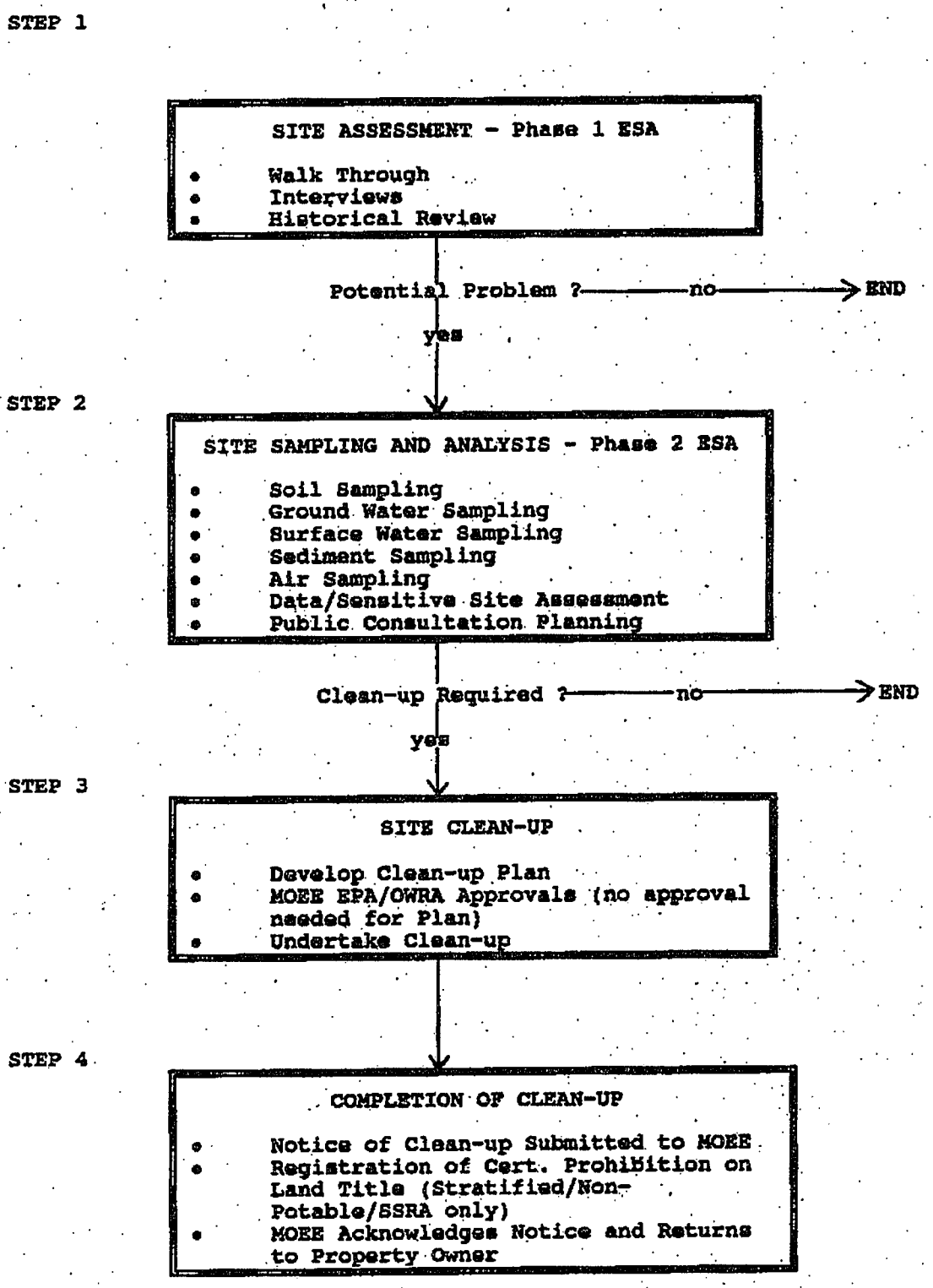


Figure 4 - Clean-up Process

Table 6 - MOEE Clean-up Criteria for Surface Soils/Potable Water

Surface Soil/ Potable Water	Soil Clean-up Criteria (µg/g)			Groundwater Criteria (µg/L)
Chemical Compound	Agricultural Land Use	Residential, Parkland Land Use	Industrial, Commercial Land Use	All Land Use Categories
Benzene	0.05	0.05	0.05	5
Toluene	1	1	1	24
Ethylbenzene	0.5	0.5	0.5	2.4
Xylene	1	1	1	300

Table 7 - MOEE Clean-up Criteria for Surface Soils/Non-potable water

Surface Soil / Non-Potable Water	Soil Clean-up Criteria (µg/g)		Groundwater Criteria (µg/L)
Chemical Compound	Residential, Parkland Land Use	Industrial, Commercial Land Use	All Land Use Categories
Benzene	0.05	0.5	1900
Toluene	1	10	5900
Ethylbenzene	0.5	5	28000
Xylene	1	5	5600

Table 8 - MOEE Criteria for Sub-Surface/Potable Water

Sub-Surface Soil / Potable Water	Soil Clean-up Criteria (µg/g)	
Chemical Compound	Residential, Parkland Land Use	Industrial, Commercial Land Use
Benzene	0.05	0.05
Toluene	1	1
Ethylbenzene	0.5	0.5
Xylene	1	1

Table 9 - MOEE Criteria for Sub-Surface Soils/Non-Potable Water

Sub-Surface Soil / Non-Potable Water	Soil Clean-up Criteria (µg/g)	
Chemical Compound	Residential, Parkland Land Use	Industrial, Commercial Land Use
Benzene	0.5	2
Toluene	10	100
Ethylbenzene	5	100
Xylene	5	50

Table 10 - Ontario Background Concentrations

Ontario Background Soil Concentrations	Soil Background Concentration (µg/g)	
Chemical Compound	Values Acceptable for Application to Agricultural Land Use	Values Acceptable for Application to Residential and Parkland Land Use
Benzene	0.002	0.002
Toluene	0.002	0.002
Ethylbenzene	0.002	0.002
Xylene	0.002	0.002

3.3 Soil Vapour Extraction

Much of the research on soil vapour extraction is dependant on the mass transfer and fluid flow through porous media. The first articles on soil vapour extraction were published in the mid-eighties. Since that time the wide variety of facets of this process have been investigated including the rates of stripping under various conditions and

numerical model development. Gasoline has been the most common contaminant used in the laboratory experimentation.

3.3.1 Fundamental Laws Governing Subsurface Mass Transfer

The effectiveness of SVE is measured by the rate of contaminant mass transfer that can be obtained. Henry's Law is used to determine the partitioning of a chemical between air and water.

$$C_{air} = H \cdot C_{water} \qquad \textbf{Equation 1}$$

C_{air} = concentration of compound in air, mg/L
H = Henry's constant, dimensionless
C_{water} = concentration of compound in water, mg/L

Henry's constant can be expressed in a variety of units. Its value can either be obtained from the literature or calculated using the following equation (Wilson and Clarke, 1994).

$$H = 0.01603\left[\frac{P_o \cdot MM}{T \cdot c_{sat}}\right] \qquad \textbf{Equation 2}$$

H = Henry's constant at temperature T, dimensionless
P_o = equilibrium vapour pressure at temperature T, mmHg
T = ambient temperature, K
MM = molecular mass, g/mol
c_{sat} = saturation concentration in water at temperature T, g/L

The maximum mass of VOC that can be removed by 1 m^3 of air, at temperature T, is given by:

$$m = \frac{MM \cdot P_o}{760 \cdot 0.08206 \cdot T} = 0.01603\left(\frac{MM \cdot P_o}{T}\right) \qquad \textbf{Equation 3}$$

m = maximum mass of VOC removed per m^3 of air , kg/m^3
MM = compound molecular mass, g/mol
P_o = vapour pressure at ambient temperature, mmHg
T = ambient temperature, K

To calculate vapour pressure as a function of temperature, the following equation can be used along with the constants found in Table 11.

$$\log_{10} P = A - 0.05223\left(\frac{B}{T}\right) \qquad \textbf{Equation 4}$$

P = vapour pressure at temperature T, mmHg
T = ambient temperature, K
A = constant
B = constant (molar heat of vaporisation), J/mol

Table 11 - Constants for calculation of vapour pressure

COMPOUND	CONSTANT A	CONSTANT B
Benzene	7.8948	33,803
Toluene	8.2910	39,082
Ethylbenzene	8.3462	42,072
m-Xylene	8.4295	43,453

Raults law (Equation 5) is used to determine the partitioning between a mixture, such as gasoline, and air. Hayden *et al.* (1994) showed that Raoults' law can be used to accurately describe the partitioning between gasoline and air in a contaminated soil.

$$p_i = x_i \cdot P_i^o \qquad \textbf{Equation 5}$$

p_i = partial pressure of contaminant I (mmHg)
x_i = mole fraction of a contaminant i
P_i^o = vapour of pure contaminant i (mmHg)

3.3.2 Rate Limited Mass Transfer

The mechanism through which volatile chemicals partition into the pore air must be identified to determine that rate at which contaminants can be removed from a soil. Two general observations have been made regarding this partitioning. Many researchers have concluded that, under the conditions they used to simulate SVE, the pore gas concentration was at equilibrium with either the NAPL phase or with the pore water (Hoag *et al.*, 1994; Baehr *et al.*, 1989; Hayden *et al.*, 1994). Many models are based on this local equilibrium assumption (LEA).

Other researchers have considered non-equilibrium or rate limited stripping of volatiles (Kearl *et al.*, 1991; Hayden *et al.*, 1994). Kearl *et al.* (1991) showed that equilibrium exists only at low air flow rates.

At later stages in soil venting, when the NAPL has been removed, mass transfer becomes a two step process: first contaminants desorb from the soil into the pore water and then volatize from the water into the gas phase. This results in non-equilibrium stripping of contaminants when concentrations have been reduced (Hayden *et al.*, 1994). There are several explanations for this behaviour including: rate limited mass transfer across the liquid-gas film boundary, rate limited transfer from the soil, interagreagate diffusion and gas flow bypassing areas of low permeability leaving pockets of high concentration (Rathfelder *et al.*, 1995).

3.3.3 Soil Organic Content

Organic matter in soil is naturally adsorptive. The rate of addition or removal of a chemical from a pure sample of an adsorptive material is determined using adsorption-

desorption isotherms. In soils, on the other hand, organic particles are mixed with inert particles and water and the effect of the organic portion of a soil, on the rate of chemical removal, becomes less intuitive.

Hayden *et al.*, (1994) found that mass recovery rate, for three different soils, was dominated by NAPL characteristics and not media properties. They used glass beads as well as soils with 0.1 and 1.65 percent organic matter. Comparison between the three media was done by reducing time to a dimensionless number and plotting the scaled time against effluent concentration. This scaling procedure is meaningful only if the air leaves the column at saturation. Baehr *et al.* (1989) showed this to be true for pore velocities higher than 200 mm/min.

$$t^* = \frac{t \cdot Q \cdot \rho_g}{M} \qquad \textbf{Equation 6}$$

t^* = scaled time
t = time, min
Q = air flow rate, L/min
ρ_g = density of contaminant, g/L
M = mass of contaminant added to column, g

The applicability of the local equilibrium assumption was also determined by Hayden *et al.* (1994). They reduced and increased the air flow rate to accomplish this. If there was no observed change in the concentration of the effluent, then an equilibrium existed. A flow rate of 9.31×10^{-3} mL/min/mm^2 was reduced to 3.44×10^{-3} mL/min/mm^2. During the first third of the experiment, no change was observed in the concentration of the effluent air. The flow reduction in the air stream was repeated towards the end of the experiment, when benzene concentration had fallen below the detection limit, and an

increase of at least four times was observed in the exit concentration. It was also observed that there was a significant time lag between the flow change and the observed concentration changes.

3.3.4 Microscopic Distribution of NAPL in the Vadose Zone

The distribution of NAPLs within the soil matrix is important to the understanding of the volatilisation of contaminants from soils. Simple models, such as capillary tubes or spherical soil particles, are often used to describe much more complicated soil structures. While these models are good conceptual starting points, knowledge of the distribution of NAPL in a three phase (soil-water-NAPL) system is essential to the determination of the mechanisms through which contaminants are removed. If the NAPL exists as blobs or lenses then it is likely that transfer will take place from the NAPL as well as from pore water surfaces directly in contact with pore air. Distribution of the NAPL as a film covering all wetted surfaces, on the other hand, could be modelled more simply.

Microscopic observations made by Hayden and Voice (1993) in a Croswell soil showed that a NAPL existed as a film coating all wetted surfaces across a wide range of NAPL concentrations. They reported that at approximately 80% of the NAPL saturation limit, the soil particle surfaces were coated and most of the pore volume was filled with the NAPL. The soil was partially drained to 20% NAPL by pore volume. At this level of saturation, the soil surfaces were again covered with a NAPL film, which was especially thick at the contact points between grains. This phenomena is known as the formation of pendular rings. The soil was drained until 99% of the NAPL had been removed. The researchers concluded from this that, in a moist homogeneous systems, a NAPL exists as a

continuous phase. They did not rule out existence of small pockets of NAPL at low residual concentrations where observations were not possible.

From this work, it can be concluded that while remediating a contaminated soil by using SVE, a point is reached when a two phase water-air system contains most of the contaminants. Johnson *et al.* (1990) calculated, that when contaminate concentrations for gasoline exceeded 500 mg/kg, in a sandy soil, a separate NAPL phase existed.

3.3.5 Residual Contaminant Concentrations

The ultimate goal of a remedial program is to reduce contaminant concentration to a target level. Residual soil concentration data are not readily available in the literature as most researchers have concentrated on the rate of removal of contaminants. Annable *et al.* (1993) did not directly analyse soil samples but determined the reduction in leaching potential in soils that had been stripped for varying lengths of time. The time taken to reduce the leachate concentrations of benzene, toluene, ethylbenzene and xylene, to less than 2 μg/L in extracted water, were 6, 24, 41 and 58 hours respectively. A sandy soil, with a porosity of 0.37, was used and the air flow rate was equivalent to 20 pore volumes per hour.

4.0 EXPERIMENTAL PROCEDURE

The experimental procedure detailed here was developed based on similar experiments presented in the literature and widely accepted standards.

4.1 Experimental Conditions

A series of bench scale experiments were conducted in the laboratory to determine the rate of removal of benzene, toluene, ethylbenzene and xylene from two types of soil using an apparatus that simulates Soil Vapour Extraction. Due to the health risks associated with the chemicals under study, all preparations of standards and stock solutions were conducted under fume hoods. All experiments were performed in a sealed and vented room, known as a negative pressure room.

A total of nine sets of experiments were conducted, each set consisted of three separate experiments which varied only with respect to the air flow rate used. Four sets of experiments were conducted using a sandy soil contaminated individually with benzene, toluene, ethylbenzene and xylene. Three further experiments were conducted using an organic soil. A mixture of all four chemicals was used in another experiment with sandy soil. The last experiment was conducted by blowing moisture saturated air through sandy soil contaminated with toluene. A summary of experiments is shown in Table 12.

4.2 Experimental Column Set-up

All stripping experiments were conducted in stainless steel columns, measuring 100 mm inner diameter by 1 m height (Figure 5). Both ends of the columns were threaded and acrylic caps were fitted to both ends of the columns. The top cap had one ¼ inch

compression fitting, produced by Parker, located in the centre and the bottom cap had two fittings, one in the centre and the other slightly off centre. The intention, at the time the columns were designed, was to use one port at the bottom as a drain for liquid and the other as a air inlet. As the laboratory studies were continued, and procedures were refined, it was found that the second inlet at the bottom cap was not needed and therefore was blocked with a stopper. All of the caps had a groove cut into them, designed to fit a 100 mm round gasket.

Table 12 - Experimental Conditions

EXPERIMENT	SOIL TYPE	CHEMICAL	AIR MOISTURE	FLOW (L / h)
1	Sand	Benzene	Dry	1.5 , 3.0 , 6.0
2	Sand	Toluene	Dry	1.5 , 3.0 , 6.0
3	Sand	Ethylbenzene	Dry	1.5 , 3.0 , 6.0
4	Sand	Xylene	Dry	1.5 , 3.0 , 6.0
5	Organic	Benzene	Dry	1.5 , 3.0 , 6.0
6	Organic	Toluene	Dry	1.5 , 3.0 , 6.0
7	Organic	Xylene	Dry	1.5 , 3.0 , 6.0
8	Sand	BTEX	Dry	1.5 , 3.0 , 6.0
9	Sand	Toluene	Saturated	1.5 , 3.0 , 6.0

The empty columns were placed on a specially designed bench which held the bottom of the column 400 mm above the floor, allowing the columns, once loaded, to be drained under gravity. Six holes were cut in the bottom shelf of the bench to allow access to the pressure fittings on the bottom caps of the columns. A middle shelf, which

consisted of two removable pieces, allowed the columns to be held securely in place. A bank of three flow meters was attached to the side of the bench.

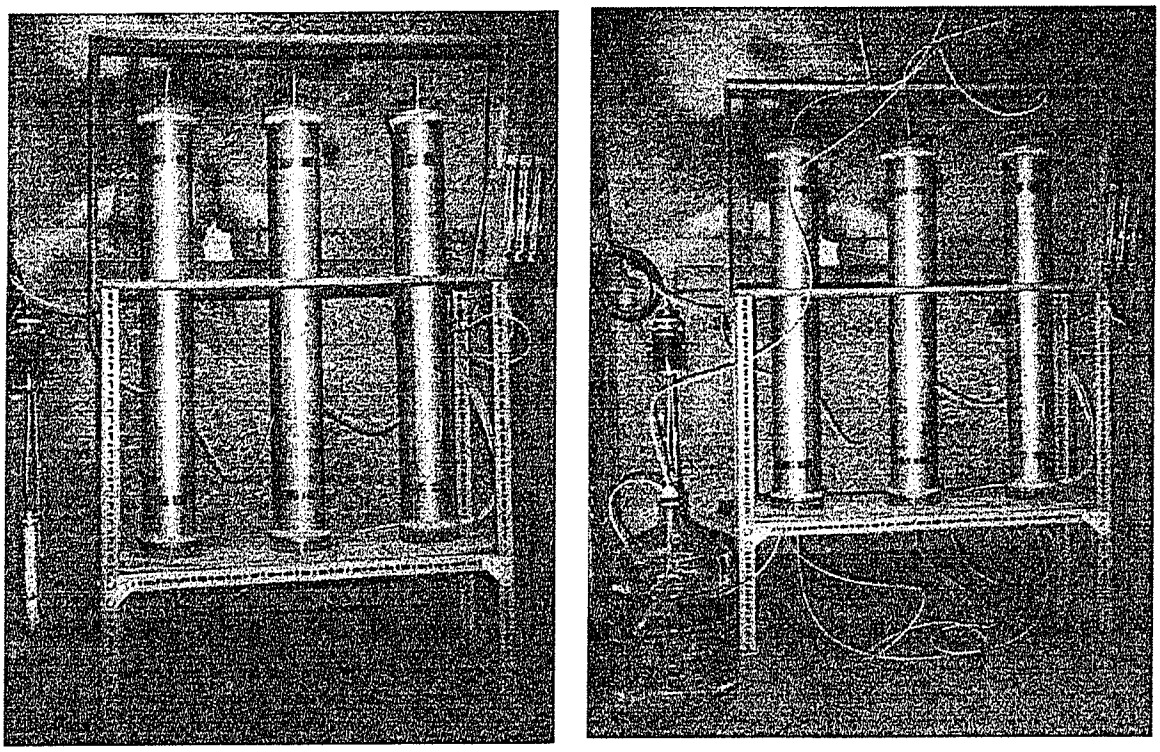


Figure 5 - Experimental Set-up

4.2.1 Column Accessories

A source of contaminant and moisture free air was needed to conduct the experiments. The air used for the experiments was the compressed air available in the laboratory. This air was typically free of both contaminants and moisture, however to ensure high quality, the air was run through a decontamination train prior to exposure to the soils. First the air was run through a bed of indicating silica gel, followed by a bed of activated carbon, both in clear glass vessels. The silica gel, which is blue when dry and pink when wet, was placed before the activated carbon because moisture would have

deactivated the carbon, rendering it useless. Visual inspection of the silica gel showed no signs of moisture break through. Also, several samples of the air leaving the activated carbon cell, taken over the course of the experiments, showed no detectable contaminants.

Following the decontamination train, the air flow was split across three flow meters. Each flow meter was calibrated using a dry test meter and the results are included on the enclosed disk. Each of the flow meters was then attached to an individual column inlet. All of the tubing in the apparatus was Teflon, which is recommended for use with the chemicals under study.

4.2.2 Soil Column Packing

Before the columns were packed with soil, they were first washed and dried. Special care was taken to ensure that the threads on both the columns and the caps were clean and free of grit to prevent damage to the caps. Three different seals were used to prevent leakage between the caps and the columns. The innermost seal was a 100 mm (4 in.) diameter Teflon 'O' ring. The second sealant was Teflon tape which was wrapped around the threading on the columns prior to placing the caps on. The final seal was silicon caulking which was applied to the outside of the cap-column interface once the caps were screwed into place.

The first step in packing a column was to screw the bottom cap on and place the column on the bench. A 200 mesh, 95 mm diameter screen was then dropped onto the bottom the column. The screens were provided by Hoskin Scientific Limited. The soil, selected for the set of experiments to be performed was then poured into the column. The column was filled in approximately 250 mm increments while tapping gently on the

outside with a mallet. A metal piece of 900 g mass was then dropped, from a height of half a meter, onto the soil, five times. This was repeated until the column was full. The top cap was then placed on the column and both the top and bottom were sealed with silicon caulking. The columns were then left for a day to allow the silicon caulking to set.

4.2.3 Preparation of Contaminant Solution

An aqueous solution of the contaminant(s) of interest was prepared and added to the soil in the column. In the experiments conducted during this study, all of the solutions were prepared at the same target concentration - 150 mg/L. This concentration is equal to the 75% of the saturation value for ethylbenzene and xylene, the least soluble contaminants studied.

In all cases, 15 L of solution were prepared in a 20 L glass carboy. Thus 2.25 grams of chemical were required to achieve the target concentration. Considering the densities of each of the BTEX chemicals, approximately 2.5 mL of neat chemical was needed to achieve the target concentration. For the experiment conducted using all four compound combined in solution a mass of 2.25 grams of each chemical were added to the carboy.

Due to the limited solubility in water of the aromatic hydrocarbons being studied, the contaminants were first added to 50 mL of methanol. Approximately 45 mL of methanol was added to a flask and then the flask was tarred, with the cap on. The target volume of neat contaminant was drawn into a 5 mL syringe, prewashed thrice with the chemical, and added to the flask containing methanol. The flask was re-weighed and the

actual mass of contaminant was recorded. The flask was then filled to the 50 mL mark with methanol.

Once the methanol solution was prepared, a magnetic stir bar was added to the carboy containing water and it was placed on a stir pad. The carboy and stir pad were placed at a height of 1.7 meters above the floor in the negative pressure room near the soil columns. The magnetic stirrer was turned on and the methanol solution was slowly added to the carboy. Immediately after the addition of any of the BTEX components to the carboy, the chemical(s) formed a separate phase, which was visible on the water surface. The carboy was then sealed with a rubber stopper and left to mix for at least an hour. Due to the lower solubility of Ethylbenzene and Xylene, these two chemicals were allowed to mix for up to four hours before they were completely dissolved.

4.2.4 Addition of Solution to the Column

Once the soil was packed and the contaminant solution was prepared, it was added to the columns. All three columns were filled with solution at the same time. A simple apparatus was constructed to accomplish this. Two lengths of Teflon tubing were passed through a stopper sized to fit the carboy. One length was cut to reach the bottom of the carboy and the other only reached a few mm into the carboy. The function of the first tube was to deliver the solution to the columns through the bottom ports. The second tube was attached to the top ports on the columns to create a closed loop system. A closed system was necessary to avoid loss of the volatile chemicals being studied. Both the delivery tube and the air return were split three ways, using 6 mm (¼ in) brass compression tees, and attached to each column at the bottom and top respectively. After

the tubing system was attached to the columns, the solid stopper covering the carboy during mixing was replaced with the pierced stopper. The carboy remained on the mixing pad 1.7 meters above the floor. A siphon was started by forcing air into the carboy using a pipette bulb attached to the air return tube. Once the siphon was started, the system was sealed and left until all three columns became saturated with solution. This typically was completed within an hour.

When the columns were saturated, the carboy was moved, without disturbing the tubing system, down to the floor and left overnight. This allowed the solution in the columns to drain into the carboy under gravity. This left the soil in the columns at its' field capacity, which is defined as the moisture content in a soil that has been drained overnight under gravity.

4.2.5 Air Flow Through the Columns

Once the columns were prepared, as described above, each column was attached to a corresponding flow meter. Both columns and flow meters were designated as A, B, and C, from left to right. The air flow rate to the system was controlled by a single valve, while the flow to each column was controlled by throttling needle valves built into the flow meters.

The air flow rates used for this study were approximately 1.5, 6 and 3 litres per hour in columns A, B, and C respectively. These flow rates corresponded to an approach velocity of 5.30E-05, 2.12E-04 and 1.06E-04 m/s. These target flow rates were set on the flow meters at the beginning of each experiment. For the five days that the experiments were run, the flow rate in each column was determined using a bubble flow meter three

times a day. It was necessary to record the flow rate periodically during each experiment for two reasons. First, the flow meters were calibrated at atmospheric pressure but because there was a pressure drop across the column, the meters were operated at a pressure higher than atmospheric. Second, there were small fluctuations in the flow rates over the duration of the experiments, possibly due to a decrease in pressure drop across the column as the soil dried.

A short length of tubing was attached to each column to facilitate the sampling of the exhaust gas from the sampling port on the top cap. Gas samples were taken directly.

4.3 Analysis of Exhaust Gas

During the course of each experiment, the rate of contaminant removal was determined by sampling the air exhausted for each column periodically. A total of thirty-four samples were taken, over a five day period, from each column. The air samples collected were analysed on a Hewlett Packard series 5890 Gas Chromatograph, equipped with a Flame Ionisation Detector, (GC/FID).

4.3.1 Sample Collection

Samples were collected using a 5 mL, gas tight, glass syringe equipped with a Mininert Teflon valve for Leurolok syringes. In all cases 1 mL samples of gas were collected for analysis. To obtain a sample, the syringe, with the valve closed, was attached to the exhaust port on the column from which the sample was being collected. The valve was then opened and the plunger was drawn up. The syringe was then removed from the port and its' contents expelled. This procedure was repeated three times, conditioning the

syringe to ensure that all traces of the previous contents were purged. A final sample was then taken, closing the valve before removing it from the exhaust port, and carried to the GC/FID for analysis.

The vast majority of the samples were analysed within fifteen minutes of sampling, but in a few cases samples were stored for up to two hours. The analysis of those samples fitted the trend seen from the other samples, leading to the conclusion that the syringes were leak free.

4.3.2 Gas Chromatography

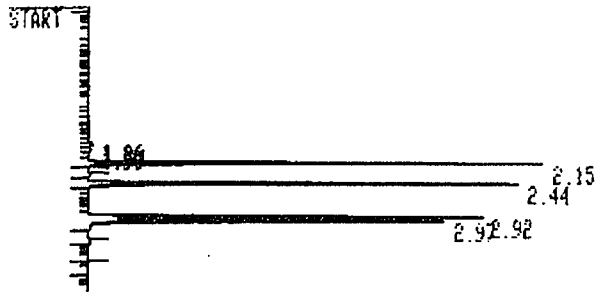
Gas Chromatography is relatively simple in concept. This technique is used to separate a mixture of chemicals so that the individual components can be identified and quantified.

The GC can be divided into three basic components or heated zones: the injection port, the column, and the detector. The purpose of the injection port is to introduce sample. A typical port is sealed with a septa through which samples are introduced.

Resolution of individual chemical is achieved in the column. Samples introduced in the injection port are carried through the column in a stream of inert gas, known as the carrier gas. The GC columns are either coated with an adsorptive material (capillary columns) or packed with a granular adsorbent (packed columns). Chemicals that have a higher affinity for the column material take longer to travel through the column, thereby increasing their retention time. Qualification of unknowns is achieved by comparing

retention times with the retention times of know chemicals. Retention times are affected by the operating conditions of each individual GC.

The final component of the GC, the detector, is used to quantify the concentration of the chemicals of interest. There are many different types of detectors available. The type used in this study was a Flame Ionisation Detector (FID). This type of detector uses a hydrogen flame to ionise the contents of the carrier gas stream as it exits the column. The detector converts the ionisation potential into an electrical signal which is outputted to an integrator. An example, shown in Figure 6, was taken from the data set generated in the study. The integrator calculates the area under the signal vs. time curve and assigns that area to the time of the signal peak. To calculate the actual concentration the GC must be calibrated with known concentrations of any chemical being analysed.



RUN # 1298
WORKFILE ID: C
WORKFILE NAME:

AREA%

RT	AREA	TYPE	AR/HT	AREA%
1.86	737	VV	0.027	0.119
1.89	1514	D VV	0.028	0.226
1.96	687	VP	0.028	0.103
2.15	180880	D PB	0.024	26.980
2.44	167630	PB	0.025	25.004
2.92	166780	PV	0.027	24.877
2.97	152190	VB	0.028	22.700

Figure 6 - GC/FID Chromatograph Resulting from the Analysis of a BTEX Standard

4.3.3 GC / FID Particulars

Each gaseous samples collected was analysed on a Hewlett Packard 5890 Gas Chromatograph. Samples were injected manually through a split/splitless injection port. Sample separation was achieved using a 60 meter capillary column, model 122-1052, manufactured by J & W Scientific. The adsorbent phase was DB1 and the film thickness was 0.25 micron. A standard Hewlett Packard Flame Ionisation Detector was used with the above GC. The output for the GC/FID was integrated and the results were printed on a Hewlett Packard model 3392A integrator.

Nitrogen, the carrier gas, was provided at a flow rate of 200 mL per minute. Hydrogen and extra dry air fuelled the FID. Both the Injection Port and the Detector were operated at 250 °C and the column was held isothermally at 100°C. The run time for the GC was four minutes, which was ample time to resolve the chemicals of interest. The integrator parameters that were used are listed below in Table 13.

Table 13 - GC/FID Integrator Parameters

PARAMETER	SETTING
Attenuation	4
Chart Speed	1.0
Peak Width	0.04
Peak Threshold	0
Area Rejection	0

4.3.4 GC/FID Operation

Before any samples were analysed on the GC/FID, the unit was turned on and left to warm up for at least one hour. This allowed the output signal to stabilise and provided sufficient time to purge any contaminants and/or moisture from the system. When ever the GC was heated, the carrier gas was always on to avoid damage the instrument.

For the injection of samples into the GC, first the syringe containing the sample was fitted with a blunt tipped needle which worked best because it caused the least wear on the injection port septa. Rheodyne KF-722 needles, supplied by Supelco, were used for this study. Once the needle was in place the syringe, with the valve still closed, was inserted into the injection port. The valve was then opened and the sample injected slowly. The syringe was held in place for several seconds with the valve open and the plunger held down. The valve was then closed and the syringe was slowly removed. Within four minutes, the results of the analysis were outputted to the Integrator and the instrument was ready to analyse another sample.

Although the method used for sample introduction was relatively simple, some problems were encountered. In order to deliver samples in a consistent manner the septa on the injection port was changed after approximately every one hundred injections. Thermolite 11 mm diameter septa (catalogue #20363) were used during the initial stages of this study. The septa often caused problems with sample injection. Fresh septa would clog the needle for the first three to five injections and occasionally after that. It was also observed that occasionally there was great resistance when samples were being injected. Upon investigation, it was found that small pieces of the septa had fallen into the injection

port, creating a plug. The injection port was cleaned and Hewlett Packard septa were used in place of the problematic septa. Once the new septa were in place, not a single problem was encountered during the several thousand samples that were subsequently run.

4.3.5 GC / FID Calibration

The calibration of the GC/FID was needed to both identify the retention time of the chemicals of interest and to calculate the response factor to obtain concentrations from area responses. In this study, the calibration for all four BTEX components was conducted using a combined standard.

The first step in generating a calibration curve was to select the appropriate range of concentrations. The primary calibration was completed using a range of approximately 0 to 100 mg/L liquid concentration. Another calibration was conducted over a range of approximately 0 to 2 mg/L to determine the lower detection limit of the method used. A final calibration was done covering concentrations up to 2,000 mg/L. This concentration was much higher than the solubility limit of all four chemicals in water, and was used to show that the calibration was indeed accurate and the response curve levelled off at the correct saturation values for all four chemicals. A flow chart outlining the method used to calibrate the GC/FID is shown in Figure 7.

Once the stock solution was prepared, aqueous standards were prepared in 10 mL volumetric flasks. For this study, aliquots of 0, 2, 4, 8, 15, 30, 60 , 125, and 250 μL were added to individual flasks containing approximately 8 mL of reagent quality water. The flasks were then filled to the 10 mL mark and inverted three times to mix the contents.

The contents of the flasks were then poured into 20 mL headspace vials, which were then sealed with Teflon caps.

The sealed headspace vials were then placed in a water bath set at 25 ∓ 0.1 °C, and left to equilibrate for 4 hours. At that time, a 1 mL sample was manually taken from each vial, one at a time, and injected into a GC/FID. The vials were sampled from lowest to highest concentration, to avoid cross contamination.

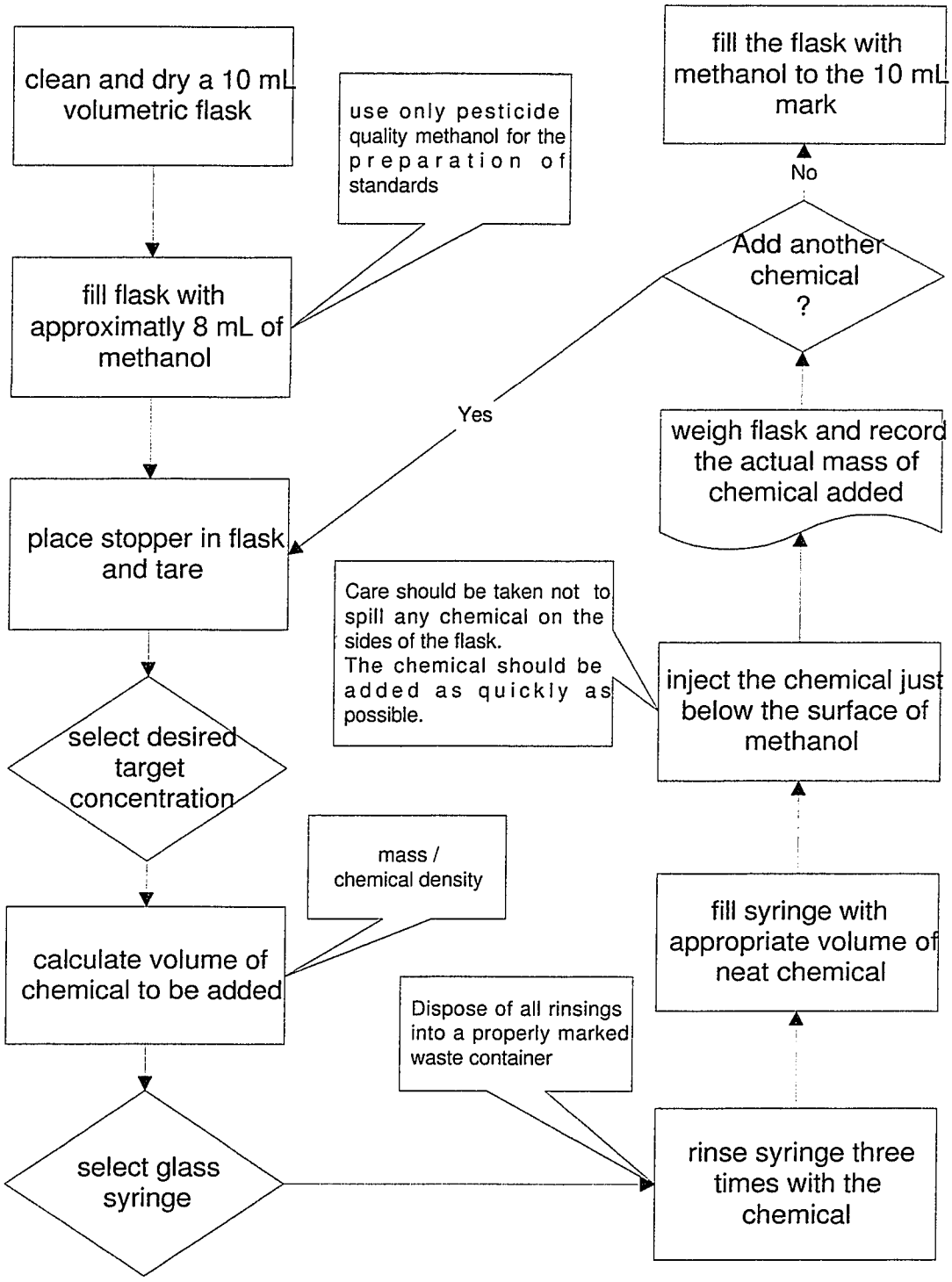


Figure 7 - Preparation of Stock Standards for Calibrations

The concentration in the headspace above the calibration standards was determined using Henry's law, knowing the temperature and the liquid concentration. It was also recognised that only 10/11 of that concentration was actually injected in the GC/FID since the syringe vial system was a closed system. Typical calibration curves for each of the four chemicals in air and water are shown in Figures 8 to 11.

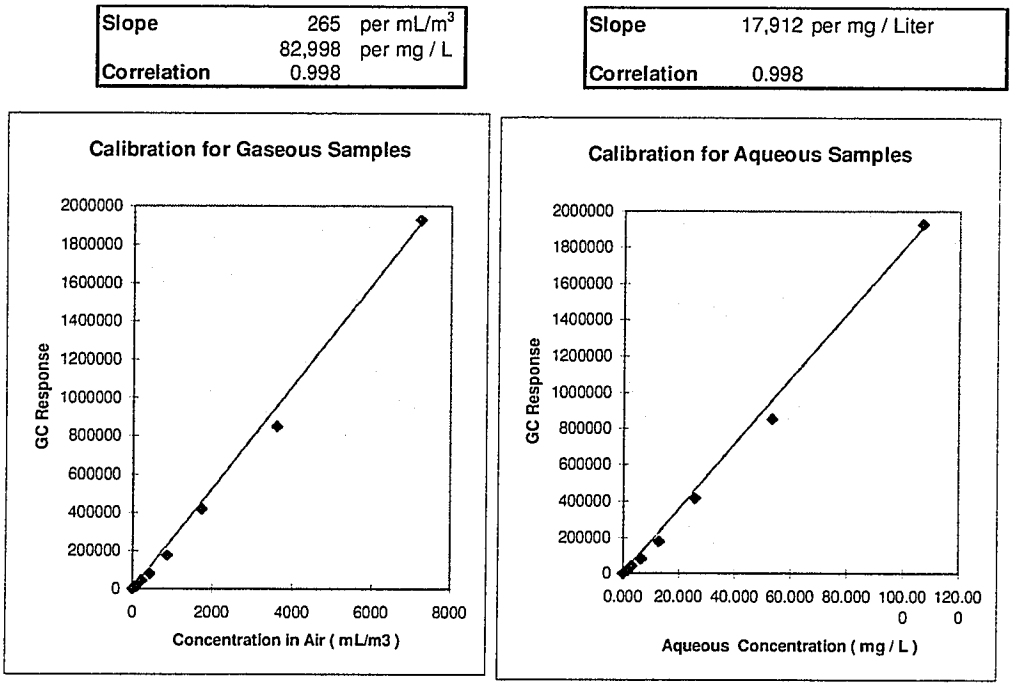


Figure 8 - GC/FID Calibration for Benzene

4.4 *Analysis of Residual Contaminant Concentrations in Soil*

At the end of each experiment soil from each column was sampled in order to determine the residual concentrations. The analysis of the soil samples was conducted on a Gas Chromatograph equipped with a Mass Spectrometer. A purge and trap system was used for sample introduction.

Slope	237	per mL/m^3
	62,979	per mg / L
Correlation	1.000	

Slope	16,527	per mg / Liter
Correlation	1.000	

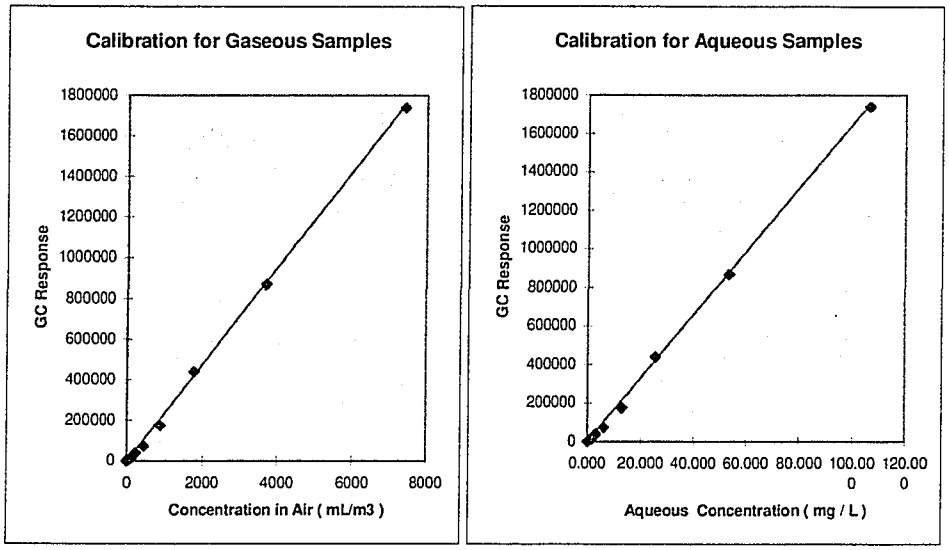


Figure 9 - GC/FID Calibration for Toluene

Slope	210	per mL/m^3
	48,304	per mg / L
Correlation	0.993	

Slope	15,560	per mg / Liter
Correlation	0.993	

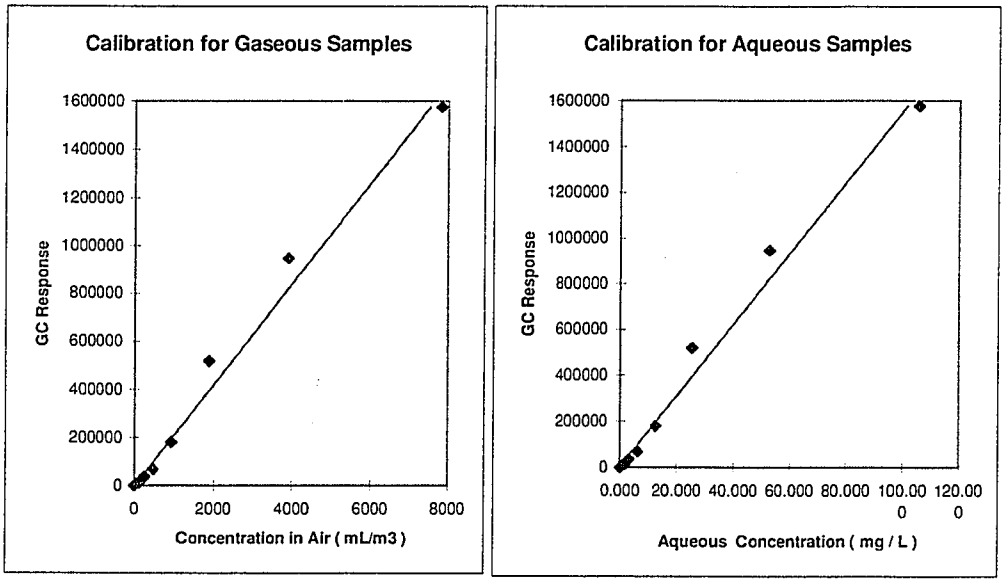


Figure 10 - GC/FID Calibration for Ethylbenzne

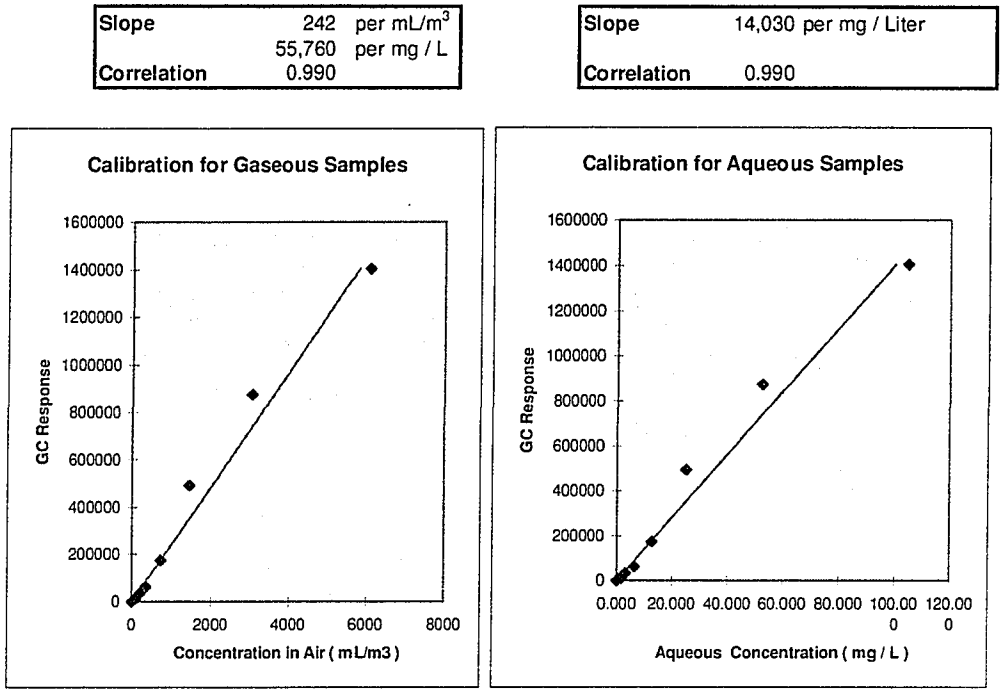


Figure 11 - GC/FID Calibration for Xylene

4.4.1 Sample Collection

At the end of each experiment, the air was turned off and the soil was removed from each column, one column at a time. The top cap of the column was removed and the column was inverted in order to slide the soil out. Care was taken to disturb the soil as little as possible. The soil was laid out on the floor and five samples were taken at roughly 0.1, 0.25, 0.5, 0.75 and 0.9 meters from the bottom (inlet side) of the soil column. The samples were placed, as quickly as possible to avoid loss of any volatiles, in 40 mL volatile organic liquid (VOL) bottles. The VOL bottles, which were made of amber glass and had Teflon lined screw caps, were used to ensure sample integrity since the samples were not

analysed immediately. The VOL bottles were filled to the top. The soil sample were then stored in a refrigerator until they were analysed.

4.4.2 GC/MS Analysis

For the analysis of the soil samples, a 5890 Gas Chromatograph supplied by Hewlett Packard was used. Samples were introduced into the GC using a Model 2016 Purge unit and a Model 2000 LSC Trap, both manufactured by ALS. All parameters pertinent to the operation of the GC and the purge and trap are listed in Tables 14 and 15. The detector used was a Model 5971A Mass Spectrometer (MS) supplied by Hewlett Packard. Hewlett Packard ChemStation software release C.01.05, running on an IBM compatible computer, controlled the system. Data from each sample run were gathered and analysed using this software.

Table 14 - GC/MS Settings

GC/MS SETTINGS	
MS Mass Range	50 - 550 amu
Initial Temperature	30 °C
Initial Time	2.00 minutes
Rate	20 °C / minute
Final Temperature	150 °C
Final Time	2.00 minutes

Purge and Trap is the recommended method of sample introduction for analysis of soils, with a practical quantitation limit of approximately 5 µg/kg wet mass (Method 8240). As the name suggests, this method of sample introduction consisted of two

fundamental parts. Samples were placed in glass purge tubes that had a volume of approximately 10 mL. At the start of the purge process the trap was set at 30°C.

Table 15 - Purge and Trap Settings

PURGE AND TRAP SETTINGS	
Standby Temperature	30 °C
Purge Time	12.00 minutes
Dry Purge Time	4.00 minutes
Cap Cool down Temperature	-120 °C
Desorb Preheat	100 °C
Desorb	4.00 minutes @ 180 °C
Injection	0.75 minutes @ 200 °C
Bake	8.00 minutes @ 225 °C
Purge Valve Temperature	100 °C
Purge Line Temperature	100 °C
Trap Valve Temperature	100 °C
Trap Line Temperature	100 °C

High purity Helium, the carrier gas used with the GC/MS, was bubbled through the purge tubes to remove volatile contaminants. The gas stream was then blow across the adsorbent trap to which the contaminants stick. Once the purge phase was completed, the injection port on the GC was cooled down to -120°C using liquid nitrogen. When the injection port reached the target temperature, the trap was rapidly heated, re-releasing the collected contaminants in the carrier gas stream. When the contaminants reached the

injection port, they were instantly frozen. In the final phase of sample introduction the injection port was rapidly heated and the volatile contents of the purge tube were injected into the GC. As the chemicals exited the GC column, each at its characteristic retention time, they were analysed by the MS. In the Mass Spectrometer, the molecules passing through it were ionised and both the mass of the ions formed, as well as the magnitude were detected and recorded by the ChemStation software.

The mass spectra for each individual chemical is unique and something is referred to as a spectral fingerprint or signature. Libraries of know spectral signatures are available as companion products to ChemStation. One of these libraries, the Wiley library, was available for use during this study. The availability of this extra tool made the job of identifying the chemicals of interest very simple and resulted in great confidence in any results obtained from the GC/MS.

4.4.3 Calibration

The GC/MS was calibrated using both an external standard and an internal standard. The GC/FID was calibrated with an external standard - a standard that was run separately from unknown samples an then used to correlate instrument response to chemical concentrations. An internal standard (IS), on the other hand, is mixed into the unknown sample and is run through the instrument with the samples. The results from the analysis of the IS were used as a measure of the sensitivity of the instrument for each individual run.

At the beginning of each week, a Standard Spectra Autotune was done on the Mass Spectrometer. This was started from the ChemStation software and involved the instrument releasing a chemical, which was stored internally, into the detector and adjusting the detector response to expected levels. Every day that the GC/MS was used, a Quick Tune was started from the software that performed minor adjustments to the instrument similar to the weekly tune.

A combined standard was used to calibrate the GC/MS for use during this work. This standard was prepared by using a procedure similar to that described earlier in Figure 7. A stock standard, containing benzene, toluene, ethylbenzene and xylene, was prepared in methanol. A secondary standard was then prepared by diluting 100 μL of stock standard into 10 mL of reagent water. The resulting concentrations are show in Table 16. The secondary standard was then used directly to prepare calibration standards.

Table 16 - Calibration Standards for the GC/MS

CHEMICAL	STOCK STANDARD (mg / mL)	SECONDARY STANDARD (μg / μL)
Benzene	8.4	8.4
Toluene	8.4	8.4
Ethylbenzene	8.0	8.0
Xylene	8.1	8.1
1,4 Dicloro-2- butane	10.1	10.1

Once the secondary standards were prepared, the GC/MS was calibrated using aqueous samples. These were prepared in a 5 mL glass syringe. The syringe was first

rinsed several times with reagent grade water. Next, it was filled to the 5 mL mark with water, and the plunger was pulled back to allow room for the addition of the standards. The internal standard, 1,4 Diclorobutane, was added to the syringe next. A 10 μL aliquot was used. Finally an aliquot of secondary standard was added to the water. The standard curve was completed by using fourteen concentrations prepared using aliquots of 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 30 and 35 μL.

The curves generated from this calibration were not linear over the entire range. Only the first five points, the minimum required, were used to calculate the instrument Response Factor. The Response Factor, shown below, was subsequently used to calculate the concentrations in unknown samples.

$$RF = \frac{A_x \cdot C_{is}}{A_{is} \cdot C_x} \qquad \textbf{Equation 7}$$

A_x = area of the characteristic ion for the compound of interest

A_{is} = area of the characteristic ion for the internal standard

C_{is} = concentration of the internal standard

C_x = concentration of the compound of interest

As described above, when chemicals pass through the Mass Spectrometer for detection, they are ionised and the mass of the fragments as well as the magnitude are recorded. For the chemicals that were analysed in this study the size, in atomic mass units (amu), of the major fragments is well documented (Table 17). The area corresponding to the primary ion was used to calculate the Response Factor and the ratio of the secondary

ion(s) to the primary was used to assure that the sample being analysed was free from interference's.

For soil samples the chemical recovery was calculated in lieu of the Response Factor. Recovery was determined by spiking a soil with a known quantity of standard chemical and subsequently analysing the sample by following the same procedure as would be followed for unknown samples. The concentration determined through the analysis of the spiked sample divided by the known concentration added is defined as the recovery. Recoveries ranging from 60% to 120% are considered acceptable. When the recoveries were calculated for the sandy soil and the organic soil, shown in Table 18, most values did not fall within the acceptable range. It is felt that the recoveries reported are still acceptable because it was observed that the internal standard area response was approximately 15% higher when analysed in the presence of methanol. Had methanol been added to the aqueous standards, used to construct the calibration curve, the recovery would have been significantly higher. The recovery for benzene, taking into account the methanol effect, is still slightly low. To improve the recovery the method could be modified to reduce the headspace in the extraction vials.

Table 17 - Atomic Mass Units of Characteristic Ions

CHEMICAL	PRIMARY ION	SECONDARY ION(S)
Benzene	78	52, 77
Toluene	92	91, 65
Ethylbenzene	106	91
Xylene	106	91
1,4-Dicloro-2-butane	75	53, 91

Table 18 - Recovery Rates of BTEX in Two Different Soils

CHEMICAL	RECOVERY RATE FROM SAND	RECOVERY RATE FROM ORGANIC SOIL
Benzene	30%	46%
Toluene	56%	57%
Ethylbenzene	56%	66%
Xylene	56%	67%

4.4.4 Sample Preparation

Typically soil samples were analysed on the day after collection but in a few cases were stored, in a refrigerator, for up to five days. Proper storage for up to two weeks is acceptable. The sample preparation and analysis method, illustrated in Figure 12, is based on EPA Method 8240, the most comprehensive available.

While it was possible to place soil samples directly in purge tubes, early attempts at doing this were messy and resulted in inconsistent results. To avoid these problems, contaminants were stripped from the soil samples using methanol prior to introduction into the purge tubes.

The first tube on the purge and trap contained only water and the internal standard. The next five tubes contained the extracted samples from one column experiment. In the second last spot was a blank soil sample, prepared in the same manner and at the same time, as the others. The last tube contained the internal standard as well as a 10 μL aliquot of standard matching the chemical expected to be present in the samples.

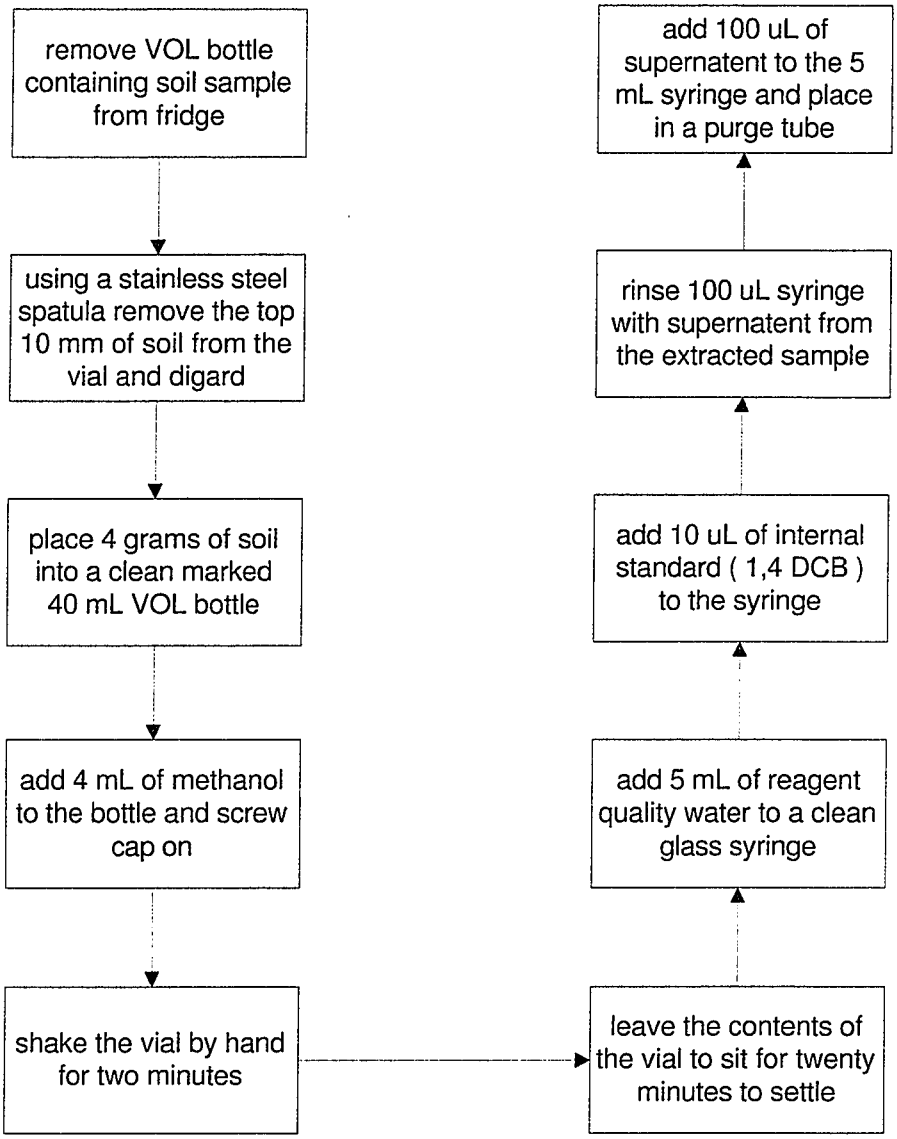


Figure 12 - Preparation of Soil Samples for Analysis on the GC/MS

4.3.5 Analysis of GC/MS Results

The output produced for each sample, run through the GC/MS will consist of a Total Ion Chromatograph (TIC), shown in Figure 13. A TIC is a plot of retention time

verses area response of the total mass passing through the detector. These plots contain the same information as those produced by the GC/FID.

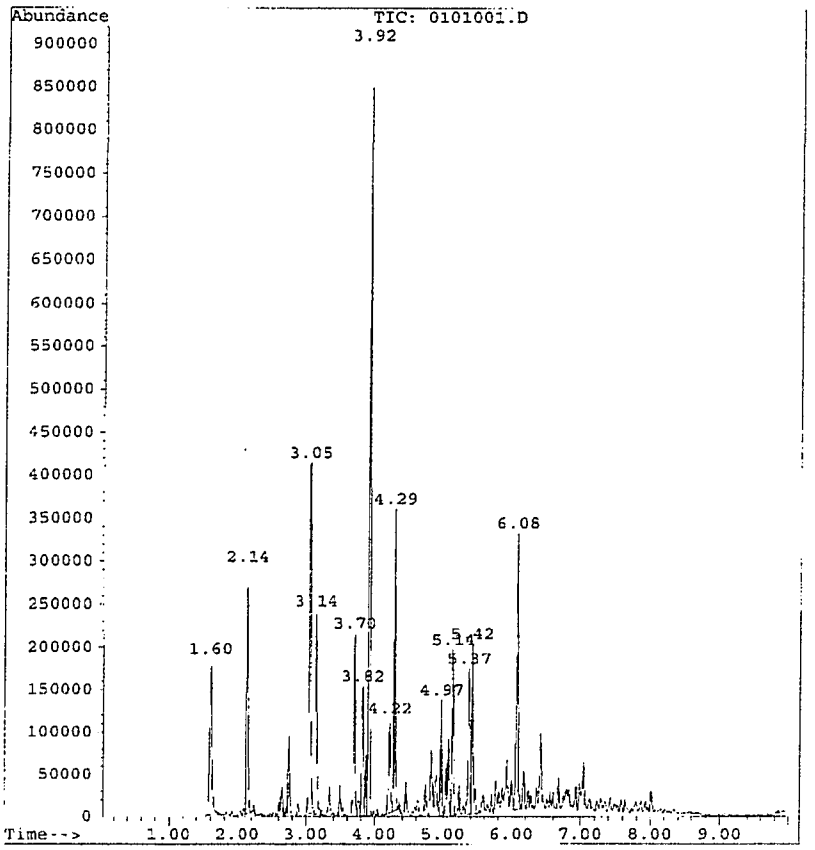


Figure 13 - A Typical Total Ion Chromatograph

To qualify the unknowns found in a sample analysed by the MS, either the retention times of peaks can be compared to known retention times or the spectral signature of peak can be matched to known signatures in the Wiley library. In this study the retention times were compared to identify the compounds of interest. The library was used to confirm these results but it was not necessary for the analysis of all the samples.

Quantification of the contents of the samples was accomplished through the use of the ChemStation software. Ion Chromatographs were extracted from the TIC, seen in Figure 14, corresponding to the Primary and Secondary Ions listed in Table 17. These Chromatographs are plots of the detector response to a small range of masses, typically one amu, versus retention time. The Ion Chromatographs, once extracted, were integrated and the area response was recorded. Two chemicals with similar retention times but different characteristic ions can be completely separated using this powerful analytical tool.

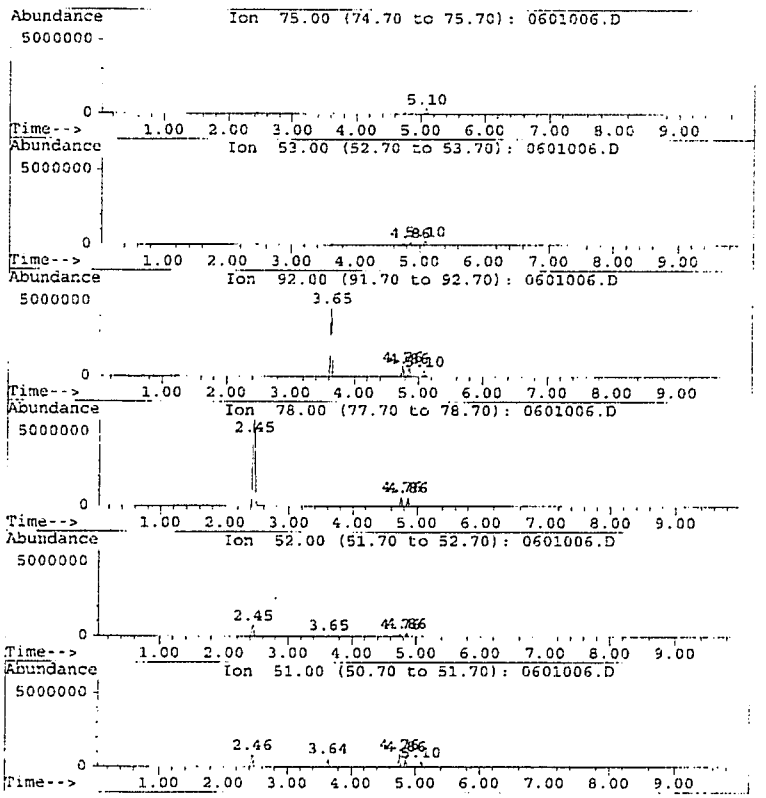


Figure 14 - Extracted Ion Chromatographs

The concentration the chemical of interest was calculated through the use of the following equation:

$$concentration\ (\mu g / kg) = \frac{A_X \cdot I_S \cdot V_t}{A_{IS} \cdot RF \cdot V_I \cdot W_S}$$ **Equation 8**

A_x = area of characteristic ion for compound of interest

I_s = mass of internal standard added

A_{is} = area of characteristic ion for internal standard

RF = response factor calculated using calibration curve

V_t = volume of total extract (4,000 µl)

V_i = volume of extract added to purge tube

W_s = wet mass of sample extracted (4.0 g)

Typical calibration curves for the four chemicals using GC/MSD are shown in Figures 15 to 18.

INTERCEPT	1.024611
SLOPE	0.134426
CORRELATION	0.994727

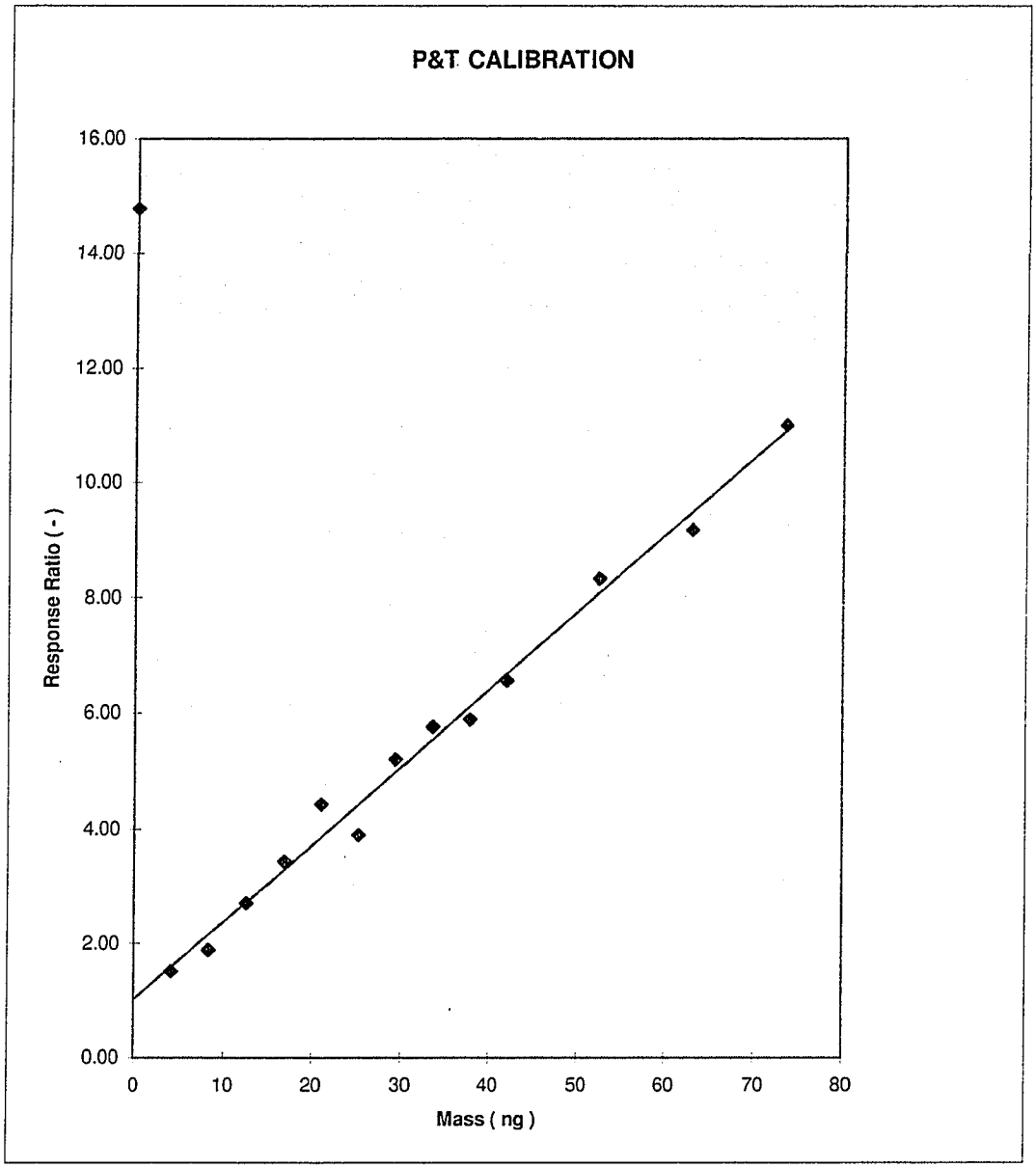


Figure 15 - GC/MS Calibration for Toluene in Organic Soil

INTERCEPT	1.500967
SLOPE	0.077323
CORRELATION	0.897554

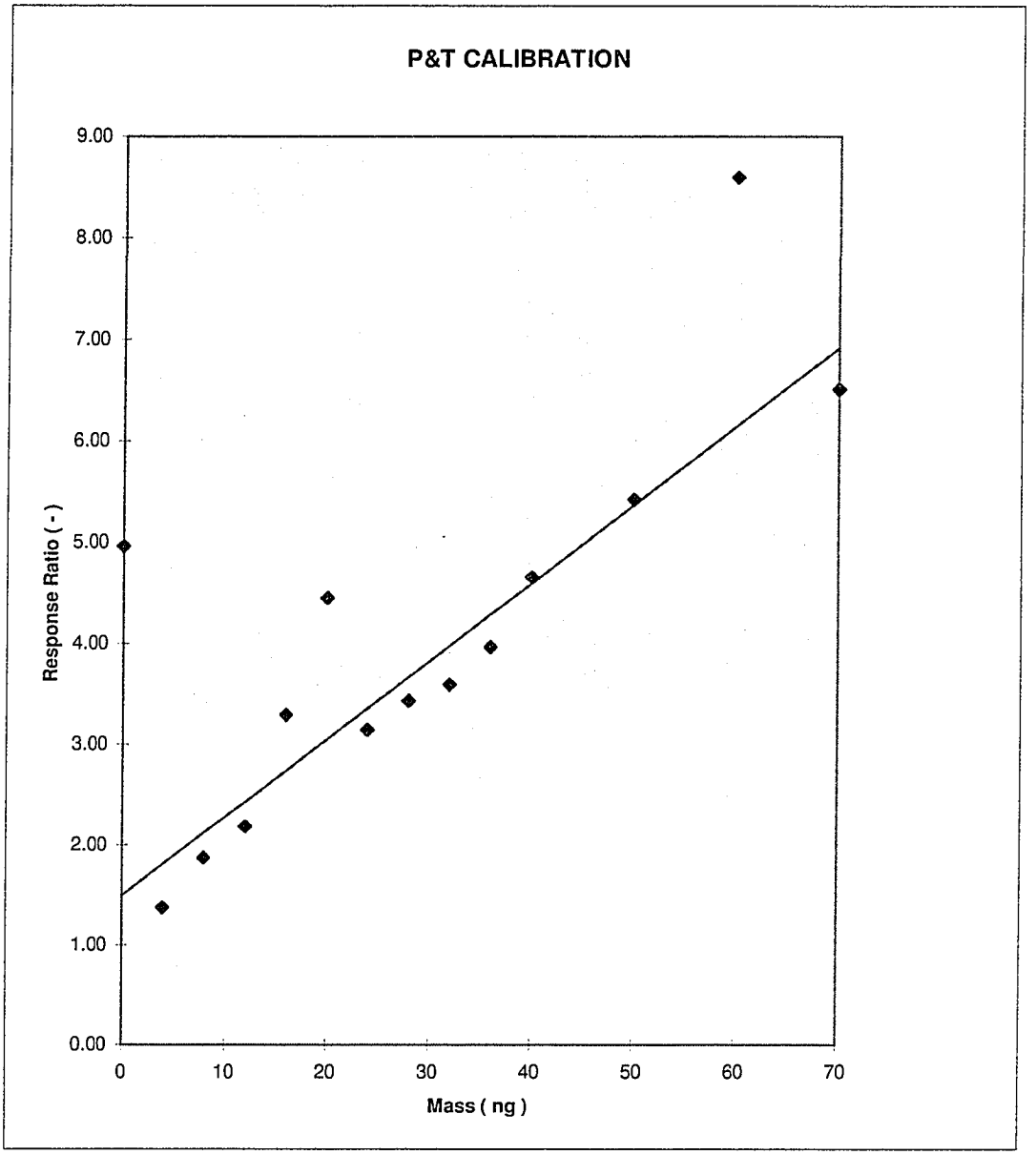


Figure 16 - GC/MS Calibration for Ethylbenzene in Sand

INTERCEPT	0.455973
SLOPE	0.087804
CORRELATION	0.99538

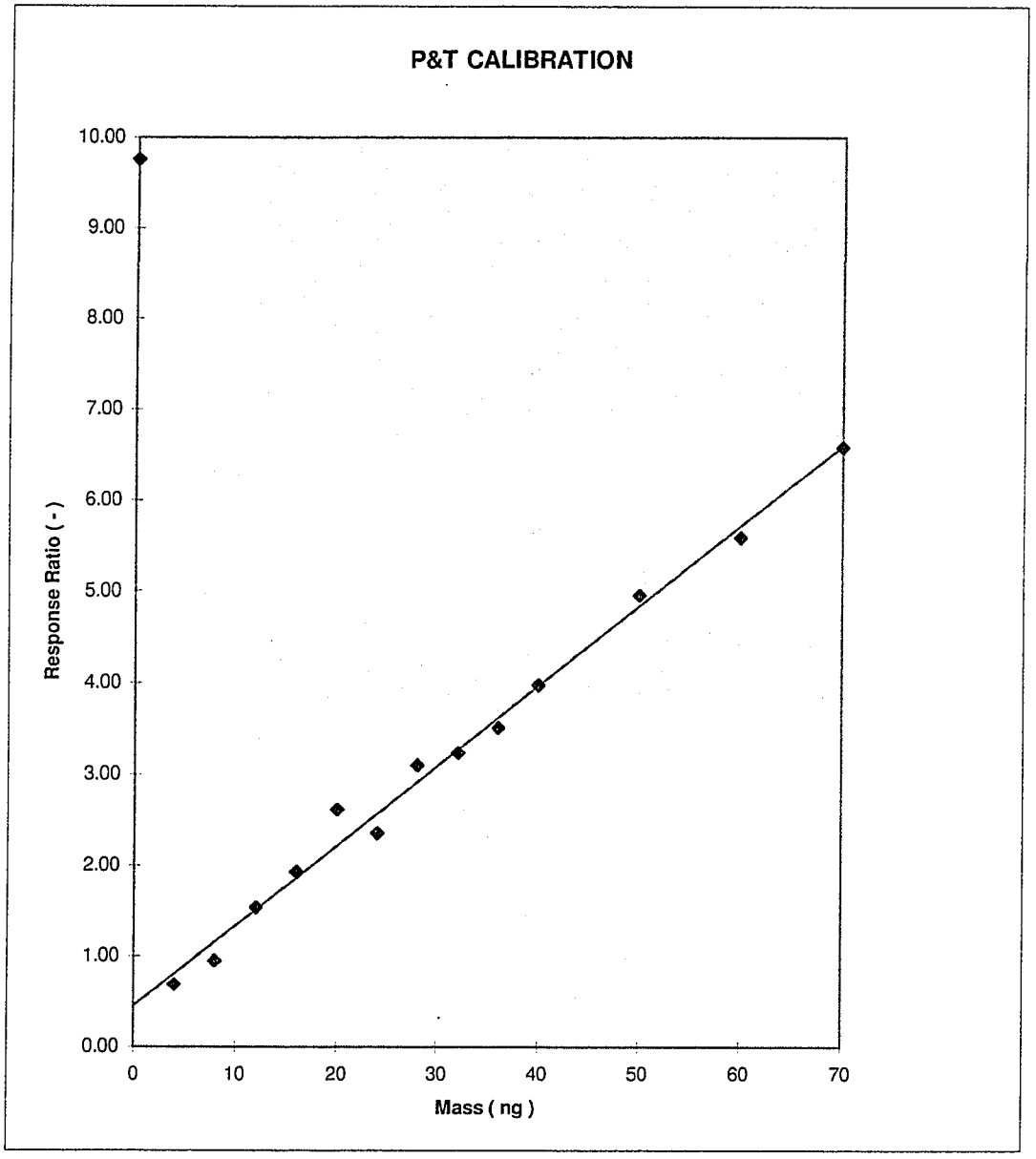


Figure 17 - GC/MS Calibration for Ethylbenzene in Organic Soil

INTERCEPT	2.372617
SLOPE	0.093644
CORRELATION	0.898524

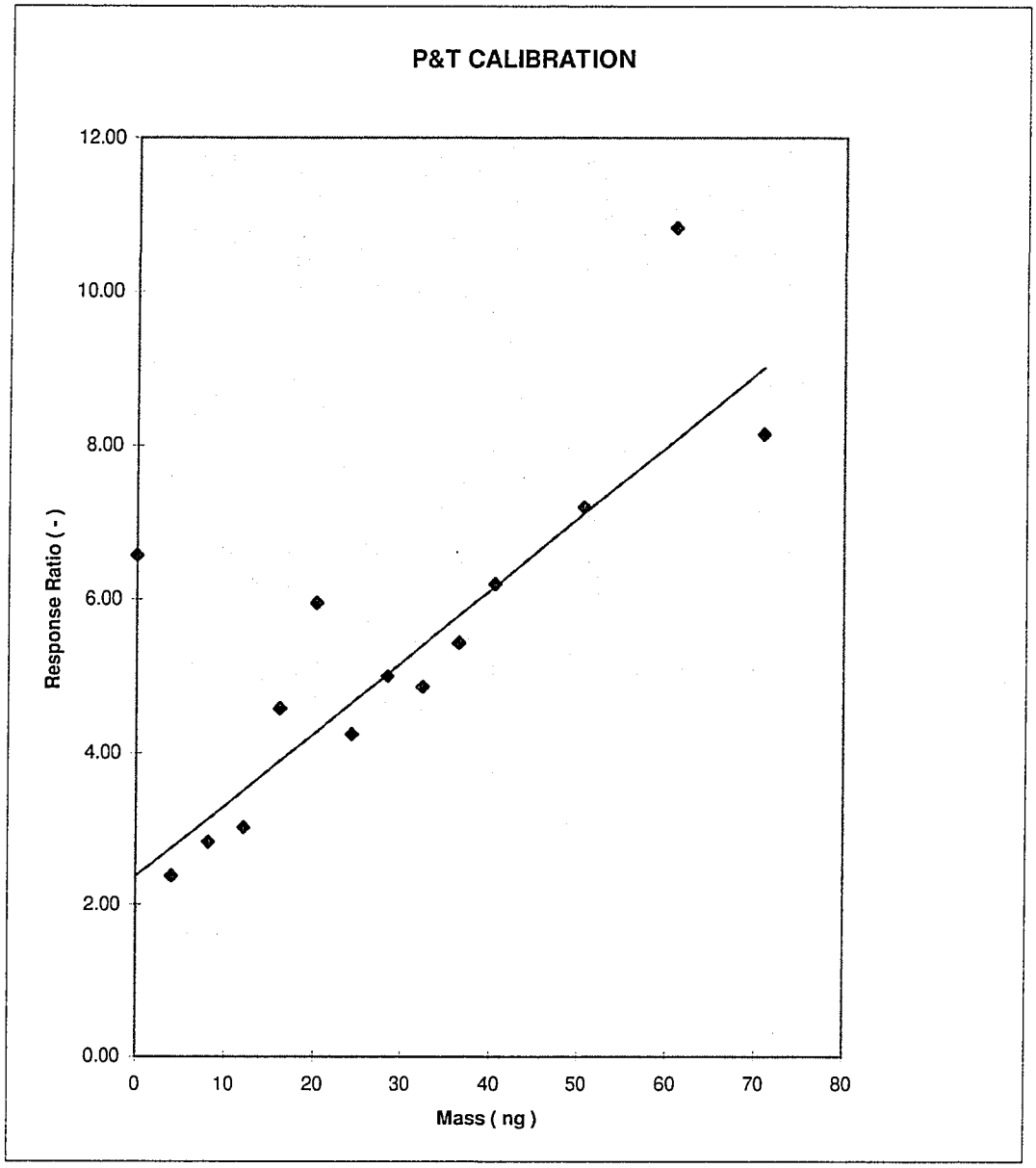


Figure 18 - GC/MS Calibration for Xylene in Sandy Soil

4.5 Determination of Soil Properties

Several soil properties were quantified for both soils used in this study. Among these properties were moisture content, porosity, ash content, which was used to calculated the organic carbon content, and finally the particle size distribution. For each set of experiments conducted, a sample of the soil was separated from the soil being added to the columns and analysed. An average of six sandy soil and three organic soil samples was determined and used in all subsequent calculations.

The sandy soil was a lake Erie washed sand while the organic soil was a sterilised top soil purchased from a local nursery. The top soil can be reproduced using ASTM method D5268 and the grain size distribution and organic content given in Table 19.

4.4.1 Moisture Content

The moisture content of each of the soil samples was determined prior to the analysis of the soil for organic content. The same procedure that was used to classify the soils was also used to determine the moisture content of the samples taken from each of the columns. The procedure followed was ASTM standard D2974 method A and the moisture content was determined using equation 9.

$$MoistureContent,\% = \frac{[(A-B)\times 100]}{B} \qquad \textbf{Equation 9}$$

A = mass as-received, gm

B = oven dried mass, gm

4.5.2 Bulk Mass Density

The bulk mass density was determined for each soil. To determine the bulk density 100 mL samples of oven dried soil were weighed. The density was determined by dividing the mass by the volume of 100 mL (Freeze and Cherry, 1979).

4.5.3 Porosity

Porosity was determined by filling a 1 L beaker with soil packed in same manner as the columns were. The beaker and soil were then tarred on a balance accurate to 1 g. Water was added until the soil was saturated. The beaker was then re-weighed. Assuming that the specific gravity of water was 1.0 the porosity was calculated by dividing the volume of water added over the total volume. The soil moisture content of the sample as received was also taken into account as shown in the equation below.

$$Porosity = \frac{volume\ of\ water}{total\ volume} + moisture\ fraction\ as\ recieved \qquad \textbf{Equation 10}$$

Although this method should work in principle (Freeze and Cherry, 1979) a second, more common, method is available (Vomocil, 1965). Equation 11 can be used to calculate the porosity of a soil sample. The bulk mass density of the soil can be determined using the method described in section 4.5.2. The particle mass density is determined by using a water-displacement test. This test involves weighing out a mass of oven-dried soil to a known amount of water in volumetric glass ware. The mass of the sample divided by the volume of water displaced by the soil is equal to the particle mass density.

$$\eta = 1 - \frac{\rho_b}{\rho_s}$$ **Equation 11**

ρ_b = bulk mass density, g/cm^3

ρ_s = particle mass density, g/cm^3

4.5.4 Organic Content

The ash content of each soil sample was determined according to the procedure shown in Figure 19. It is based on ASTM standard D2974 method C. The ash and organic carbon content were determined using equation 12.

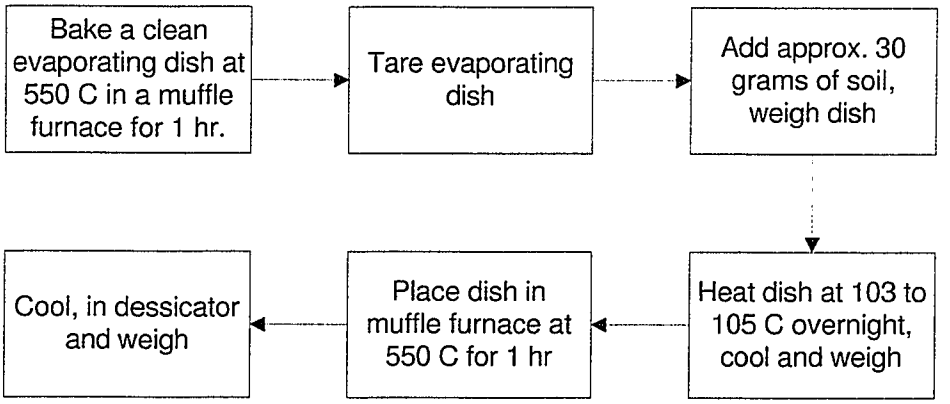


Figure 19 - Measurement of Organic Content in Soil

$$AshContent,\% = \frac{(C \times 100)}{B}$$

$$OrganicContent,\% = 1 - AshContent$$ **Equation 12**

C = ash, gm

B = oven dried mass, gm

4.5.5 Grain Size Distribution

The grain size distribution was determined for both the soils used in this study. The procedure that was followed was ASTM method D422. The resulting curves are shown in Figures 20 and 21.

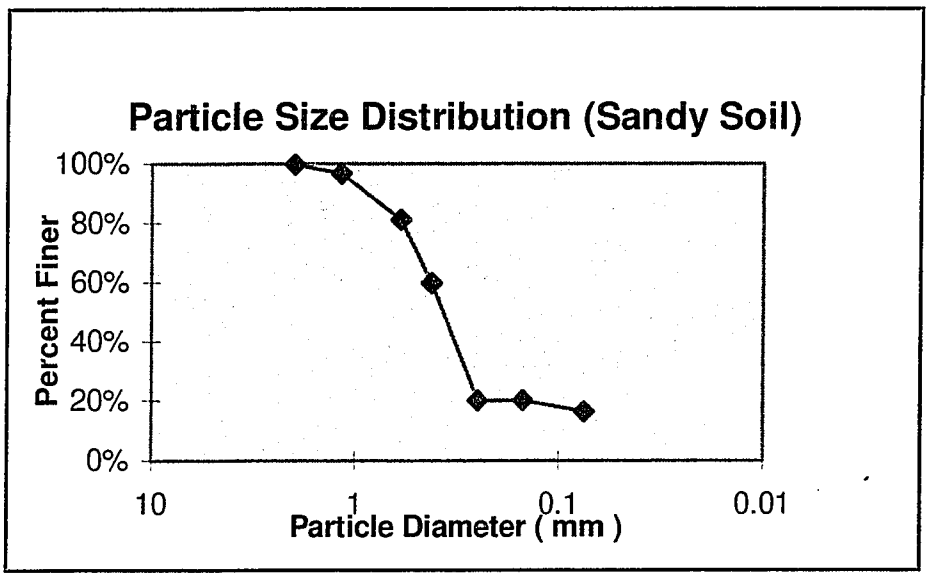


Figure 20 - Particle Size Distribution for Sandy Soil

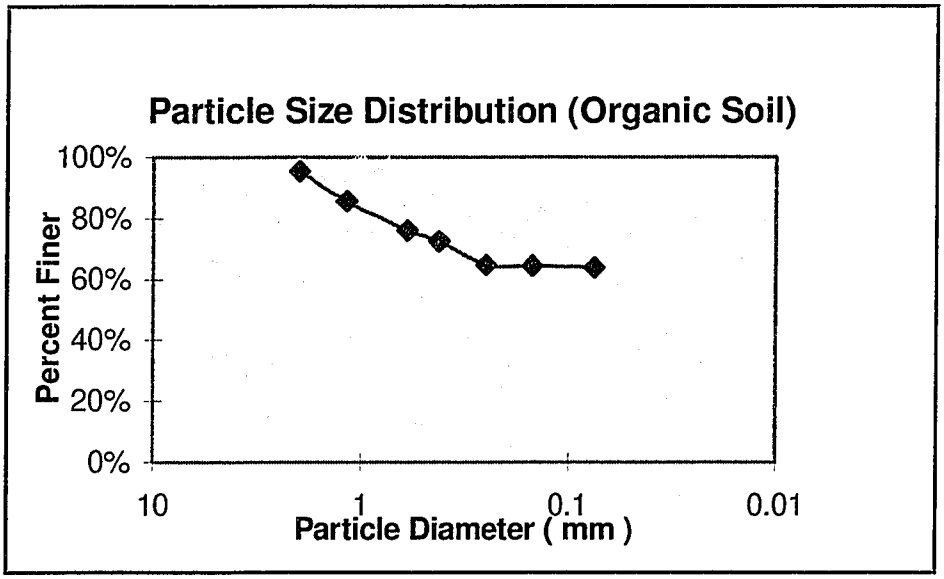


Figure 21 - Particle Size Distribution for Organic Soil

5.0 RESULTS AND DISCUSSION

Soil properties were determined and used, in conjunction with concentration data, to determine the contaminant stripping rates, the mass fraction removed and the residual contaminant distribution for the experiments conducted during this study.

5.1 Soil Characteristics

The effective porosity, organic content, bulk density and moisture content (as received) were determined by averaging six measurements for sandy soil and three measurements for the organic soil. The results and standard deviations are presented in Table 19. The average values were used in all the calculations during data analysis.

Table 19 - Soil Properties

PROPERTY	SANDY SOIL	ORGANIC SOIL
Effective Porosity, %	32.7 ± 0.6	67.8 ± 6.4
Organic Content, %	1.6 ± 0.1	24.3 ± 1.55
Bulk Mass Density, g/cm^3	1.626 ± 0.031	0.647 ± 0.003
Particle Mass Density, g/cm^3	2.416 ± 0.046	2.009 ± 0.007
Moisture Content , % (as received)	0.2 ± 0.01	30.4 ± 3.5

5.2 Stripping Rates

The effluent concentrations, from each column, were measured 32 times over the 5 day duration of each experiment. The results were recorded in a table, similar to the one shown in Table 20, which contains the results of the experiment conducted using toluene in a sandy soil. The retention times and the GC-FID response were directly obtained from

the GC analysis of the effluent gas samples. Exhaust concentrations were calculated by multiplying the GC response by the calibration factor for toluene. Mass flow rate is a product of the effluent concentration and the volumetric flow rate. The mass removed during any discrete time interval was determined by averaging the mass flow rates at the beginning and end of the interval and multiplying resulting value by the time interval and the recorded air flow rate. A cumulative total of the mass removed from each column was generated by summing the mass removed during each discrete interval. The number of pore volumes was calculated by dividing the total pore volume by the volumetric flow rate. Determination of the number of pore volumes of air that had been passed through a sample was used to compare extraction rates in dissimilar soils.

The change in exhaust concentration with time observed for toluene stripped from sand is shown in Figure 22. The solid line is the first order fit to the data set.

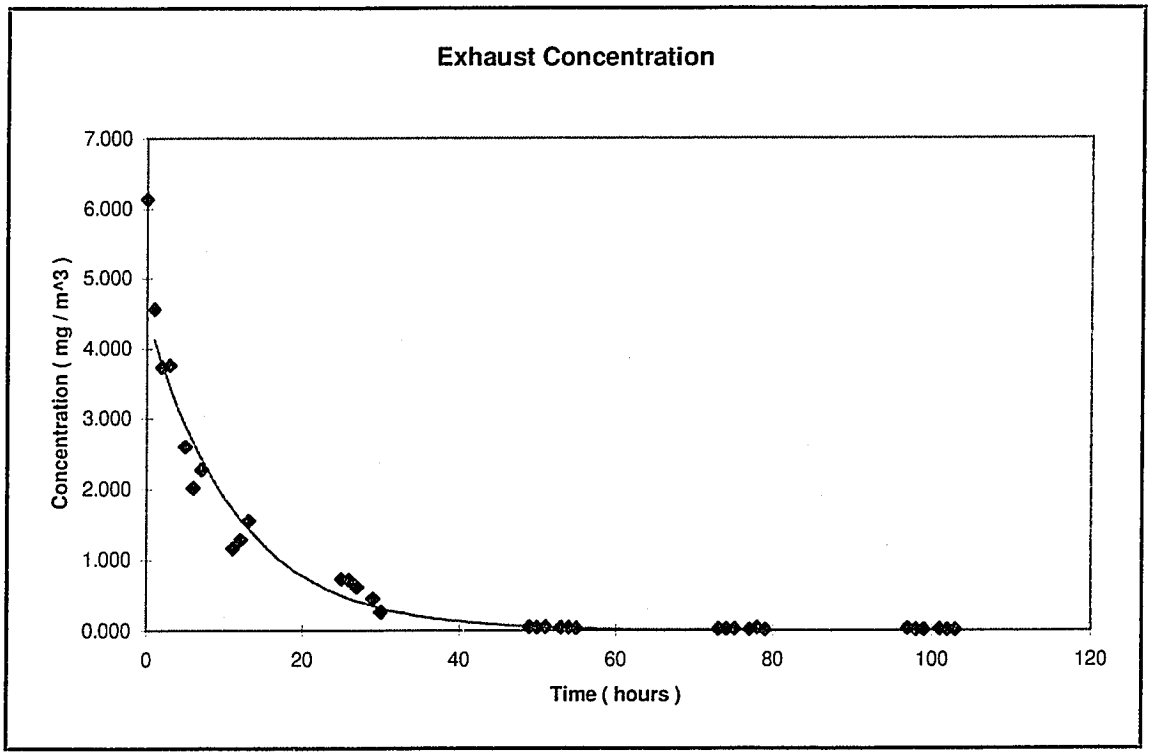


Figure 22 - Exhaust Concentration of Toluene Stripped from A Sandy Soil

Table 20 - Worksheet for Toluene in a Sandy Soil

Time (hours)	*Retention Time* (minutes)	*GC - FID Response* (unitless)	*Exhaust Concentration* (mg / litre)	*Mass Flow Rate* (mg / hour)	*Cum. Mass Flow* (mg)	*Pore Volumes* (unitless)	*Time* (hours)
0	2.44	125,220	1.988	0.000	0.000	0	0
1	2.44	93,010	1.477	2.144	1.072	1	1
2	2.44	76,098	1.208	1.754	3.021	1	2
3	2.43	76,644	1.217	1.767	4.781	2	3
5	2.44	53,155	0.844	1.225	7.773	3	5
6	2.44	41,071	0.652	0.947	8.859	3	6
7	2.44	46,424	0.737	1.070	9.867	4	7
11	2.43	23,766	0.377	0.548	13.103	6	11
12	2.44	26,249	0.417	0.605	13.679	7	12
13	2.43	31,729	0.504	0.731	14.347	7	13
25	2.44	14,947	0.237	0.166	19.734	14	25
26	2.45	14,697	0.233	0.164	19.899	15	26
27	2.43	12,652	0.201	0.141	20.051	15	27
29	2.43	9,352	0.148	0.104	20.296	16	29
30	2.43	5,501	0.087	0.061	20.379	17	30
31			spoiled				31
49	2.44	1,040	0.017	0.012	21.070	27	49
50	2.44	869	0.014	0.010	21.081	28	50
51	2.45	1,049	0.017	0.012	21.091	28	51
53	2.44	802	0.013	0.009	21.112	30	53
54	2.44	807	0.013	0.009	21.121	30	54
55	2.44	744	0.012	0.008	21.129	31	55
73	2.48	471	0.007	0.005	21.252	40	73
74	2.46	527	0.008	0.006	21.257	41	74
75	2.46	462	0.007	0.005	21.263	42	75
77	2.45	398	0.006	0.005	21.273	43	77
78	2.45	876	0.014	0.010	21.280	43	78
79	2.45	394	0.006	0.004	21.287	44	79
97	2.45	738	0.012	0.008	21.404	53	97
98	2.45	309	0.005	0.004	21.410	54	98
99	2.44	284	0.005	0.003	21.413	55	99
101	2.44	479	0.008	0.005	21.422	56	101
102	2.44	271	0.004	0.003	21.426	56	102
103	2.44	376	0.006	0.004	21.430	57	103

The cumulative mass removed was calculated by multiplying the linear average of the last two concentration measurement by the difference in time between the measurements. This created a few jumps in the cumulative mass curves but generally proved to be a reasonable assumption.

The cumulative mass removed, for toluene extracted from a sand column, is shown in Figure 23.

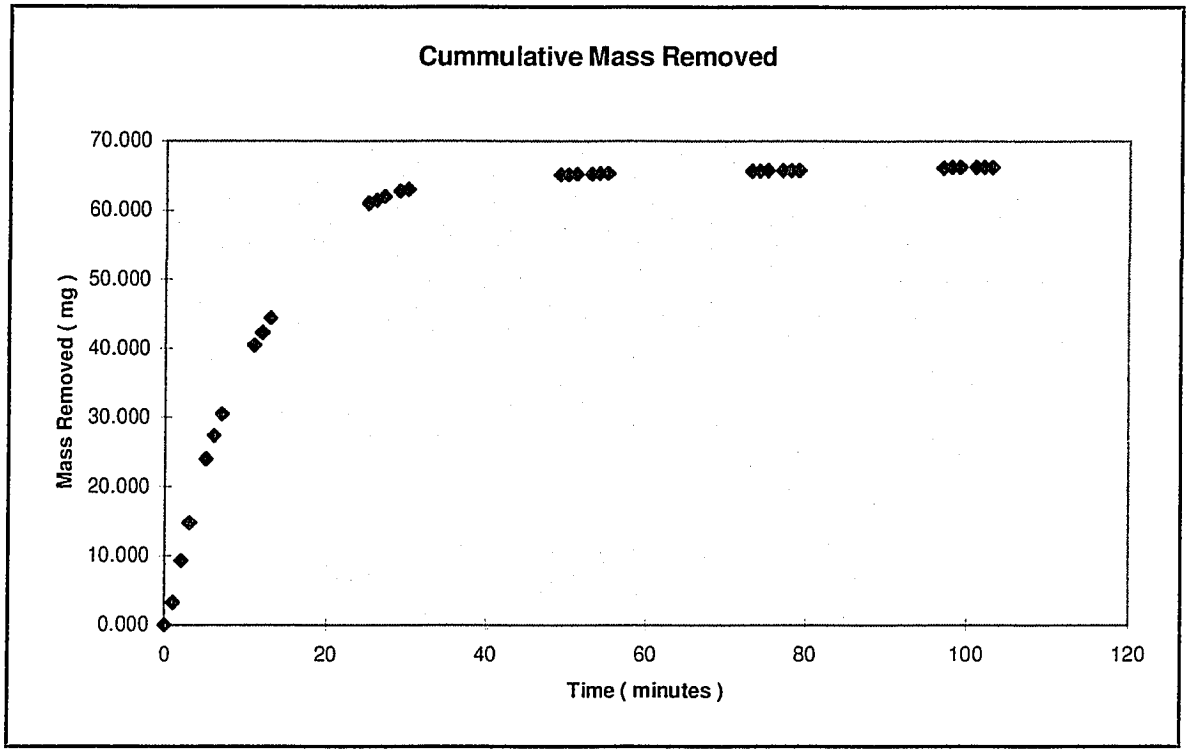


Figure 23 - Cumulative Toluene Mass Removed from a Sandy Soil

5.2.1 Concentration versus Time

The changes in contaminant concentration in the exhaust air stream, C, with time, t, was used to determine the stripping rate in a given soil at a given air flow rate. Figures 24 to 56 show typical pattern for stripping of each contaminant. The complete set of data for each column experiment are available on the disk enclosed with this thesis.

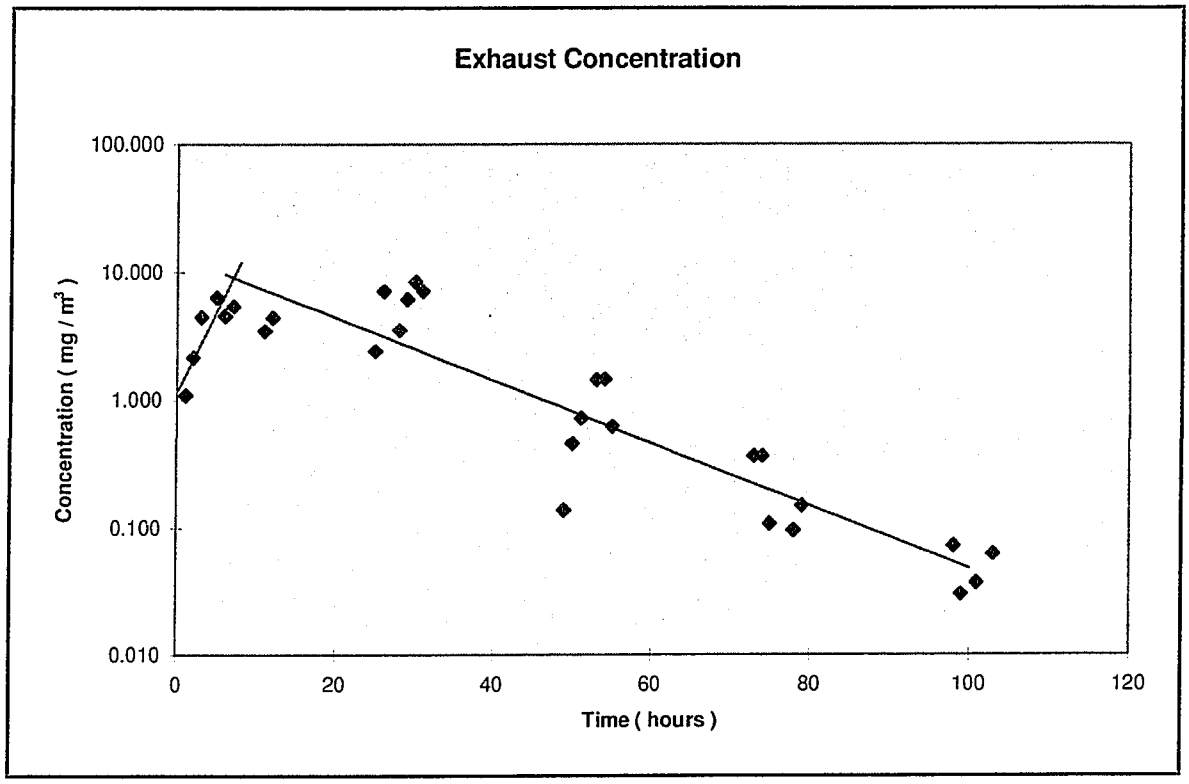


Figure 24 - Concentration of Benzene vs. Time in Sandy Soil (Q_{air} = 1.67 L/h)

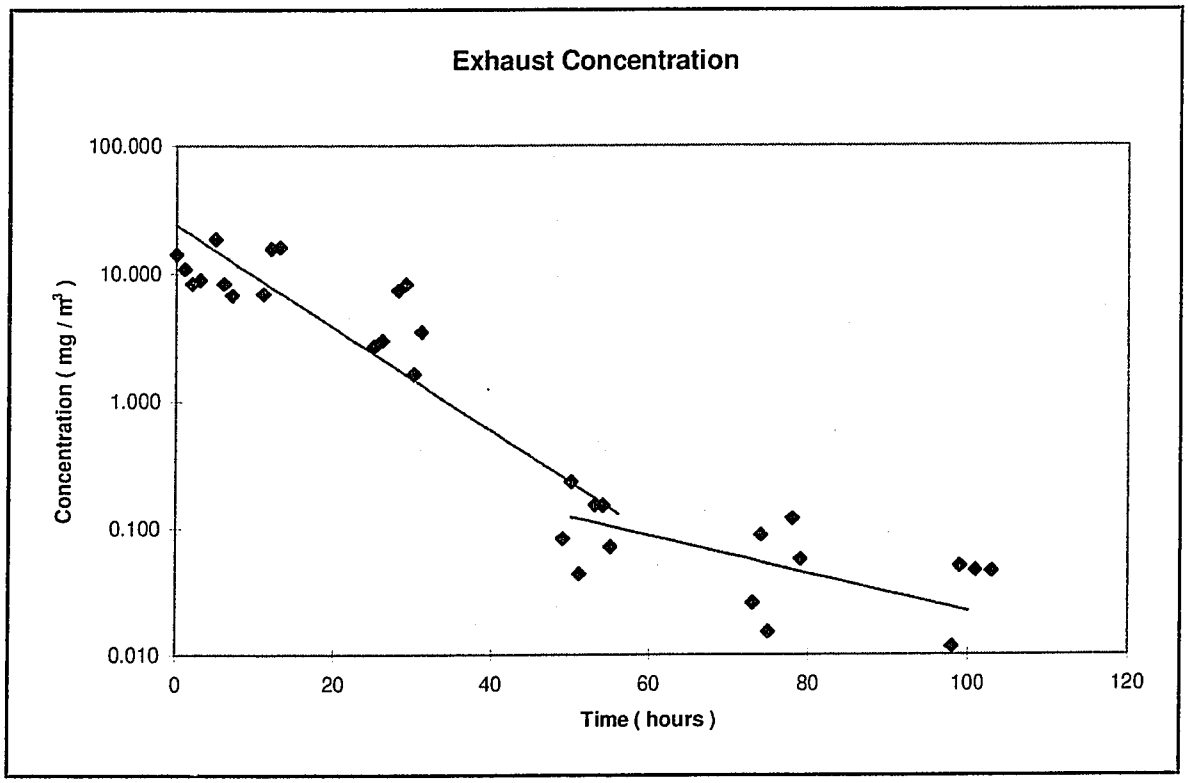


Figure 25 - Concentration of Benzene vs. Time in Sandy Soil (Q_{air} = 3.30 L/h)

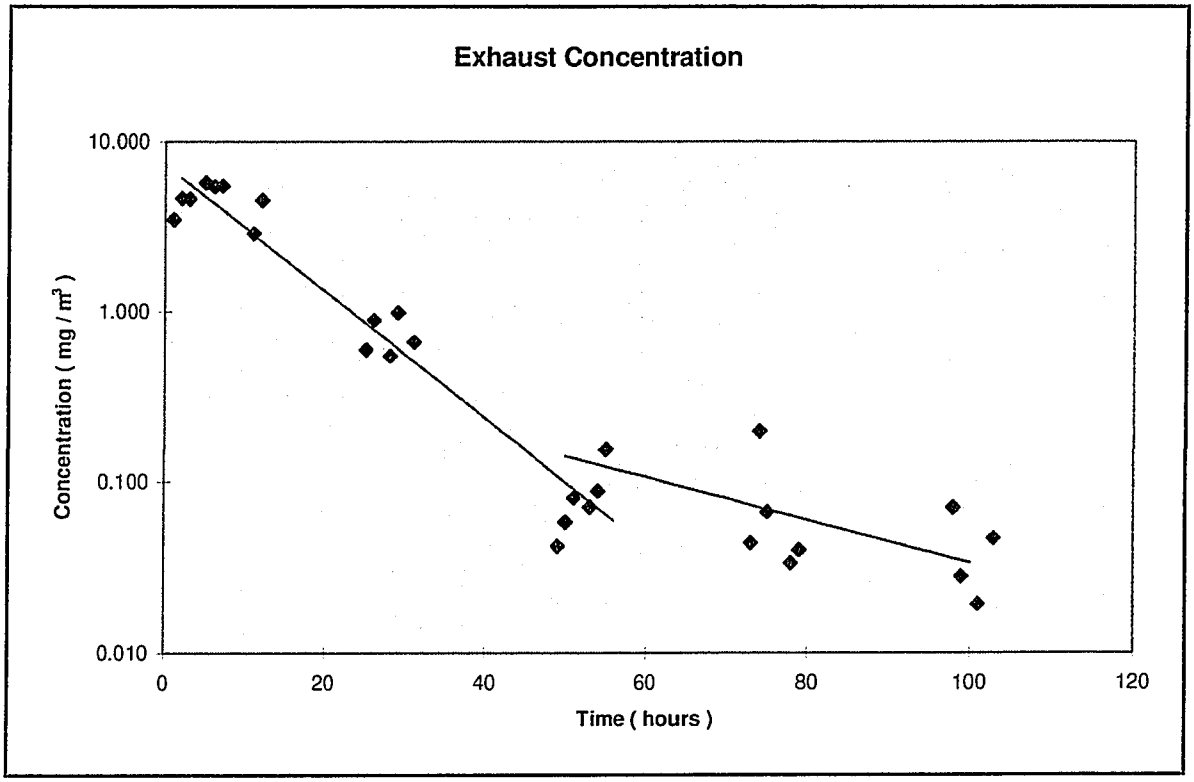


Figure 26 - Concentration of Benzene vs. Time in Sandy Soil (Q_{air} = 6.71 L/h)

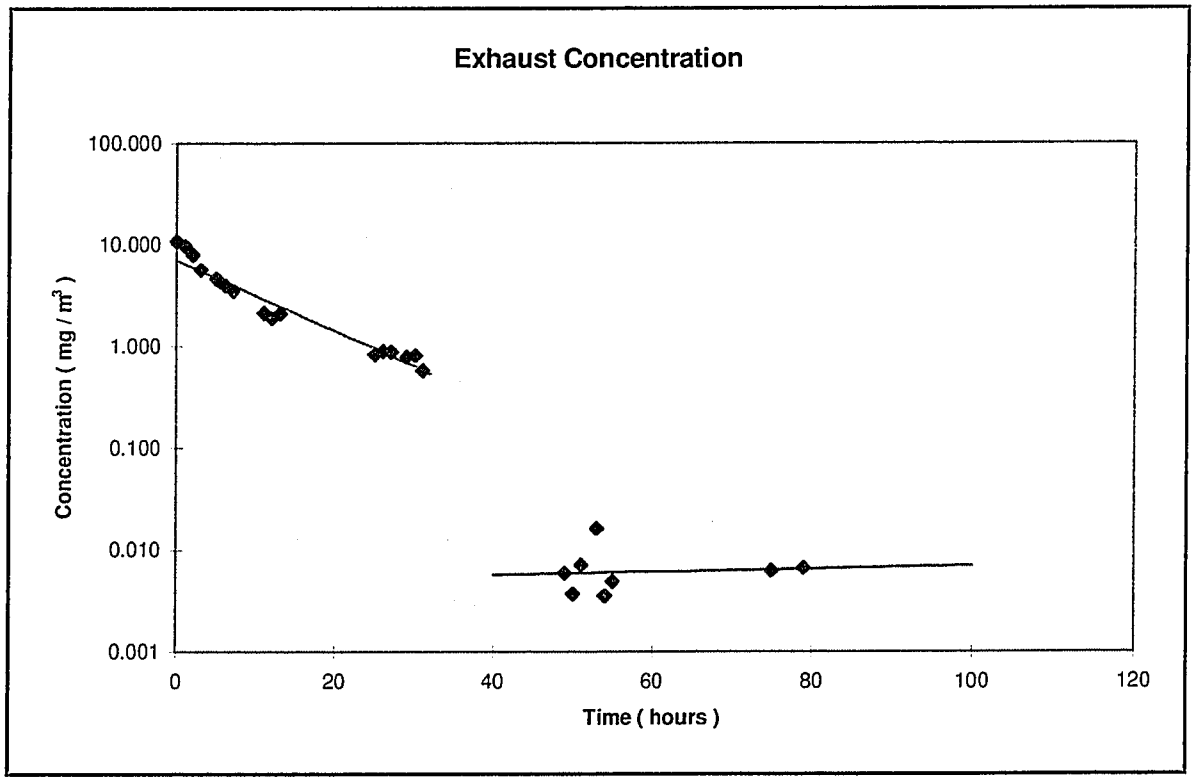


Figure 27 - Concentration of Benzene vs. Time in an Organic Soil (Q_{air} = 1.52 L/h)

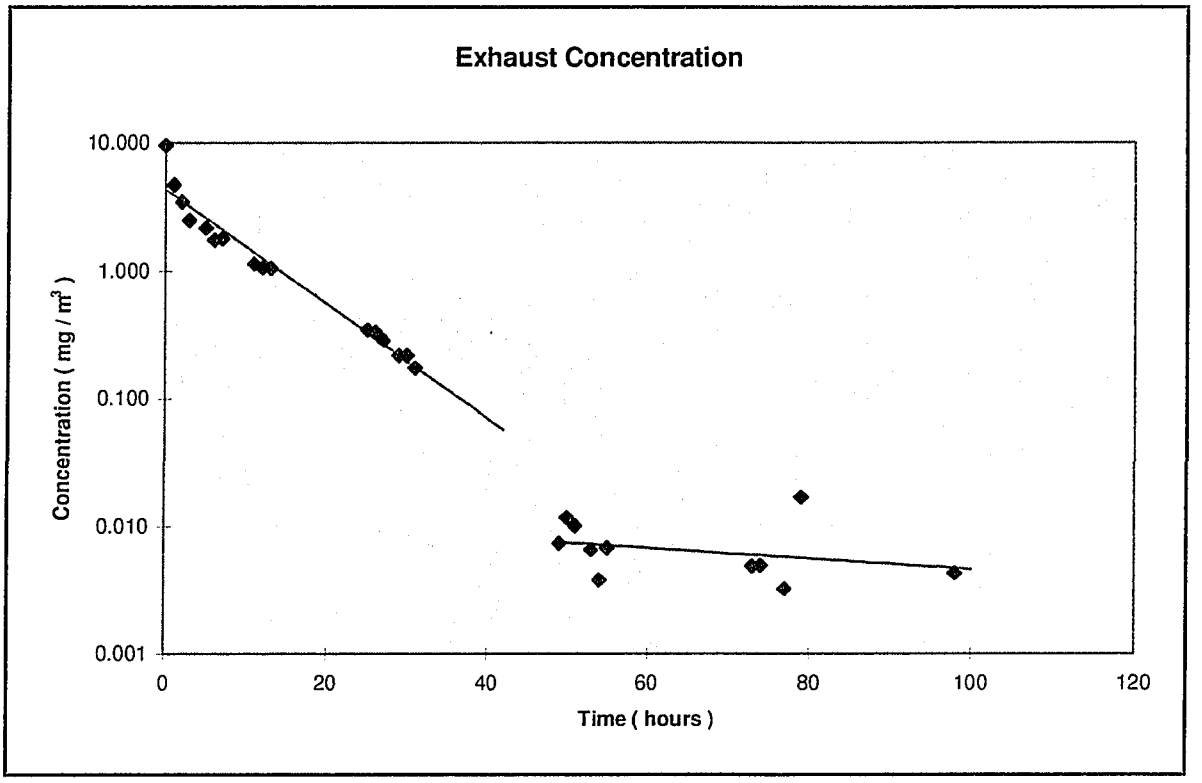


Figure 28 - Concentration of Benzene vs. Time in an Organic Soil (Q_{air} = 3.36 L/h)

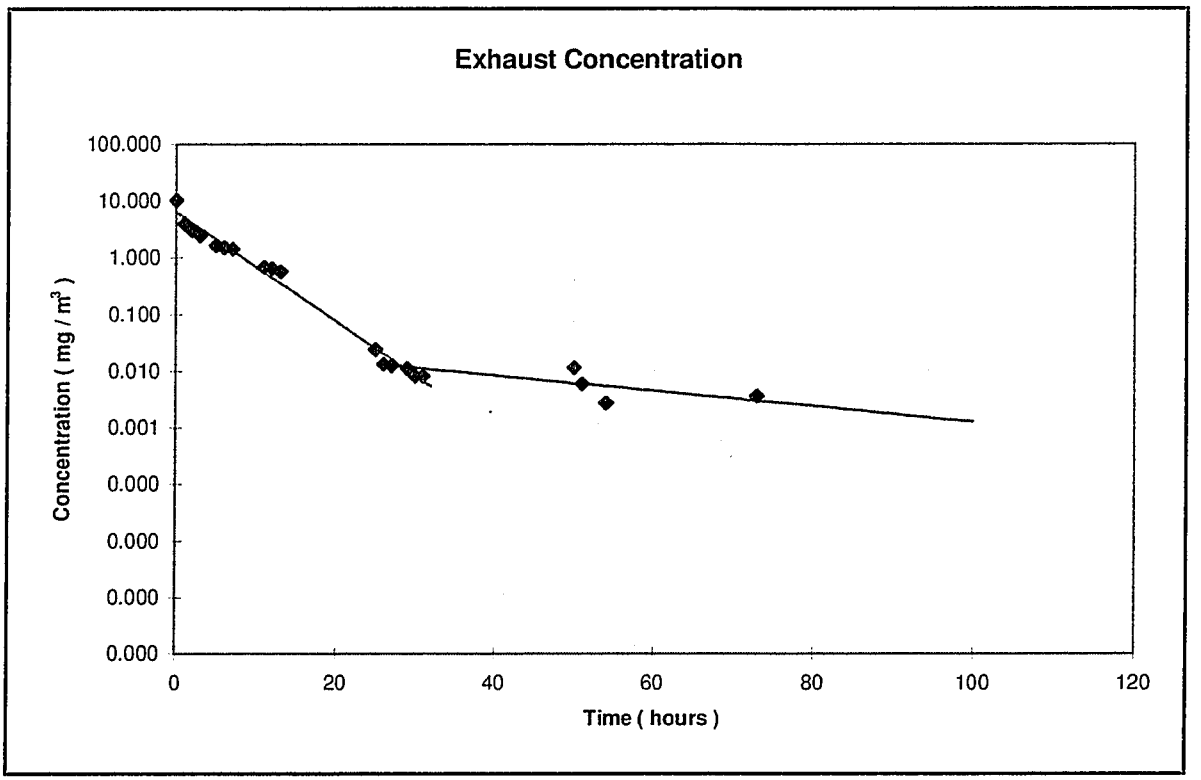


Figure 29 - Concentration of Benzene vs. Time in an Organic Soil (Q_{air} = 6.10 L/h)

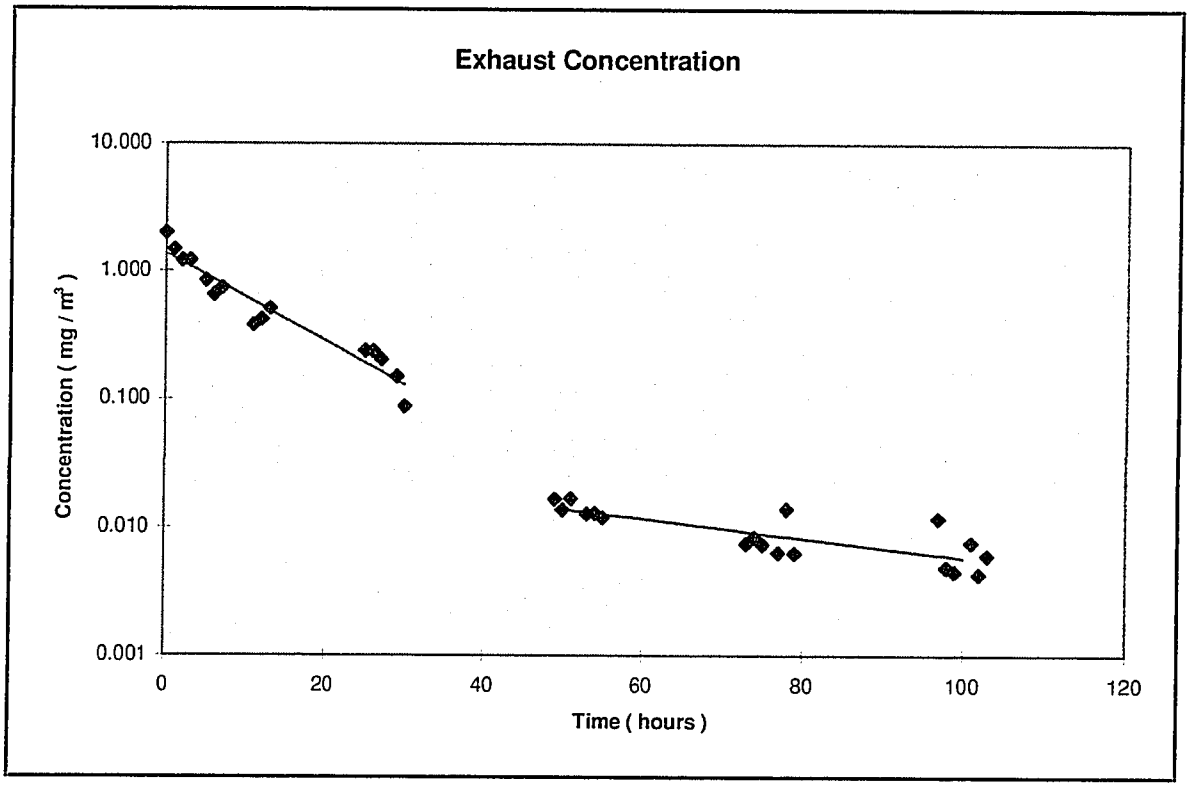


Figure 30 - Concentration of Toluene vs. Time in a Sandy Soil (Q_{air} = 1.42 L/h)

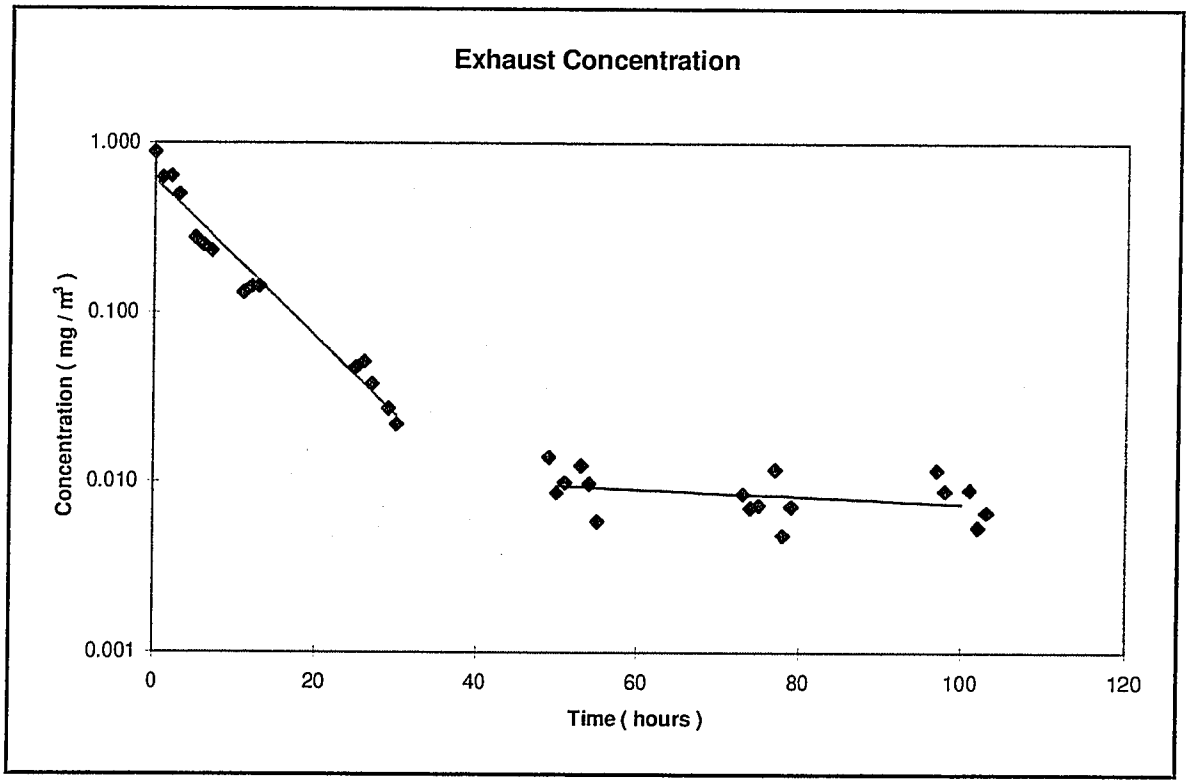


Figure 31 - Concentration of Toluene vs. Time in a Sandy Soil (Q_{air} = 3.22 L/h)

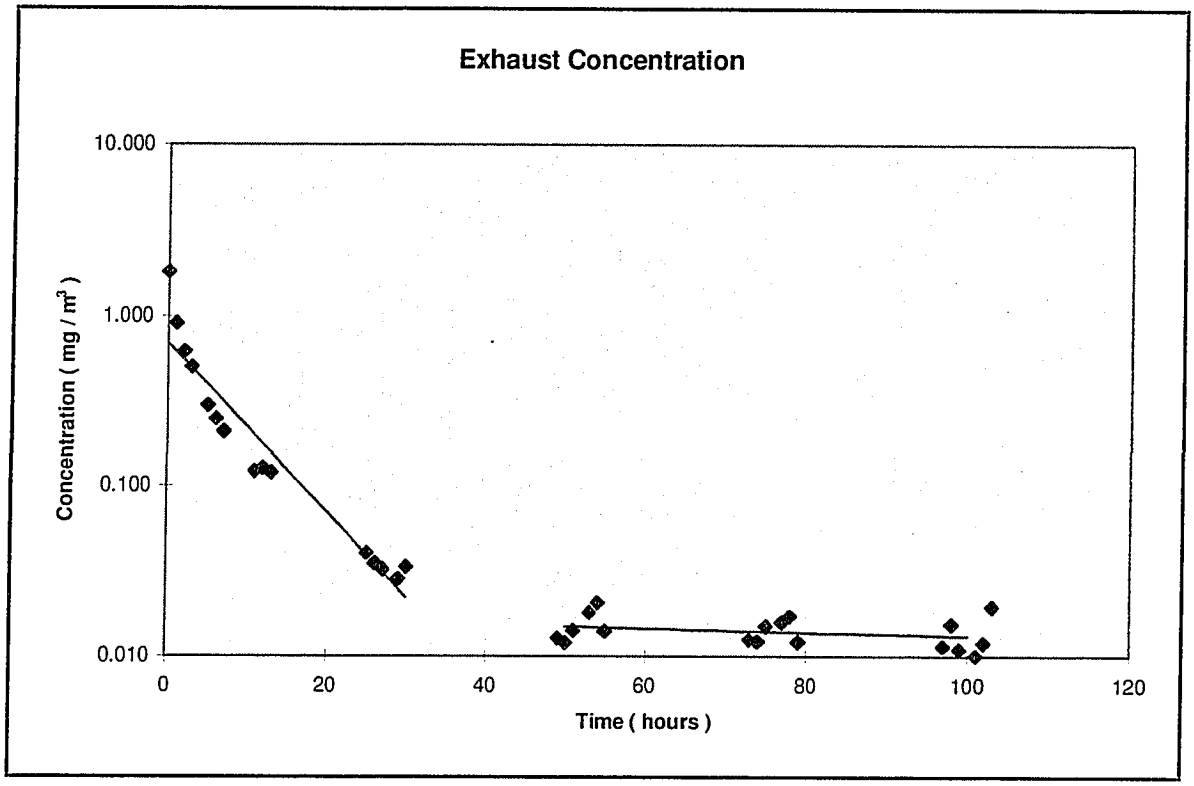


Figure 32 - Concentration of Toluene vs. Time in a Sandy Soil (Q_{air} = 5.36 L/h)

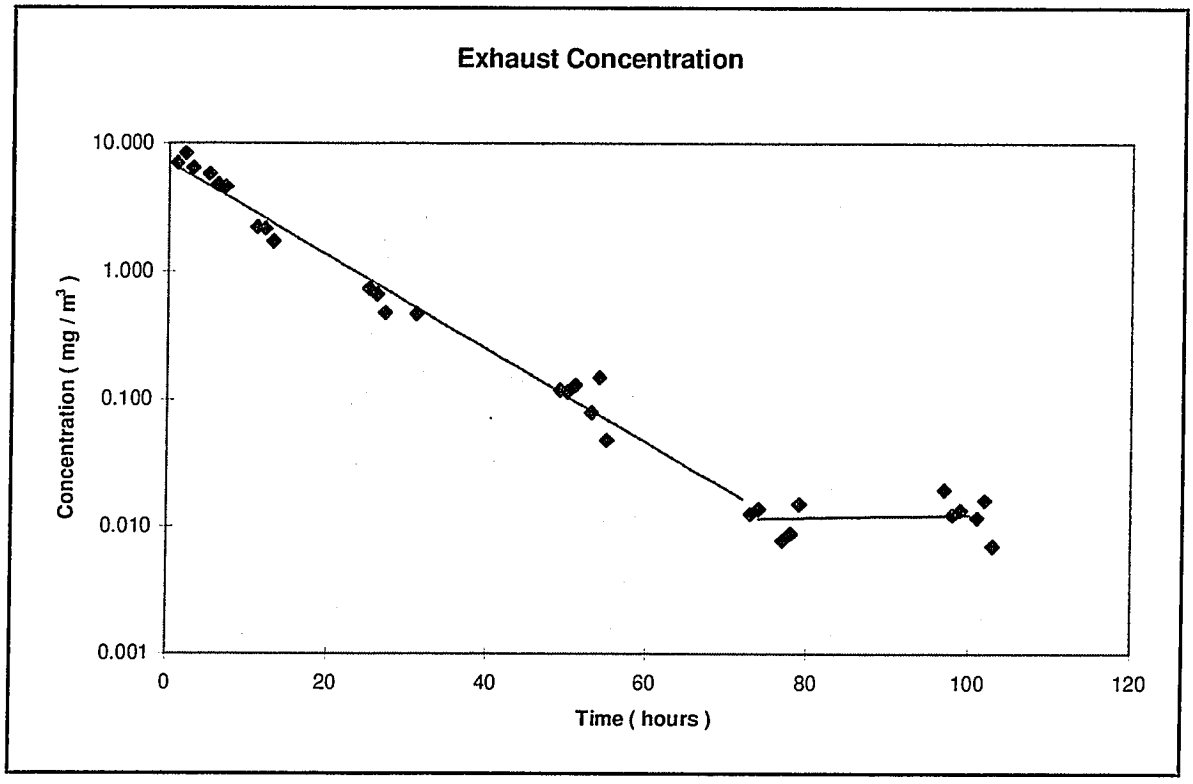


Figure 33 - Concentration of Toluene vs. Time in an Organic Soil (Q_{air} = 1.62 L/h)

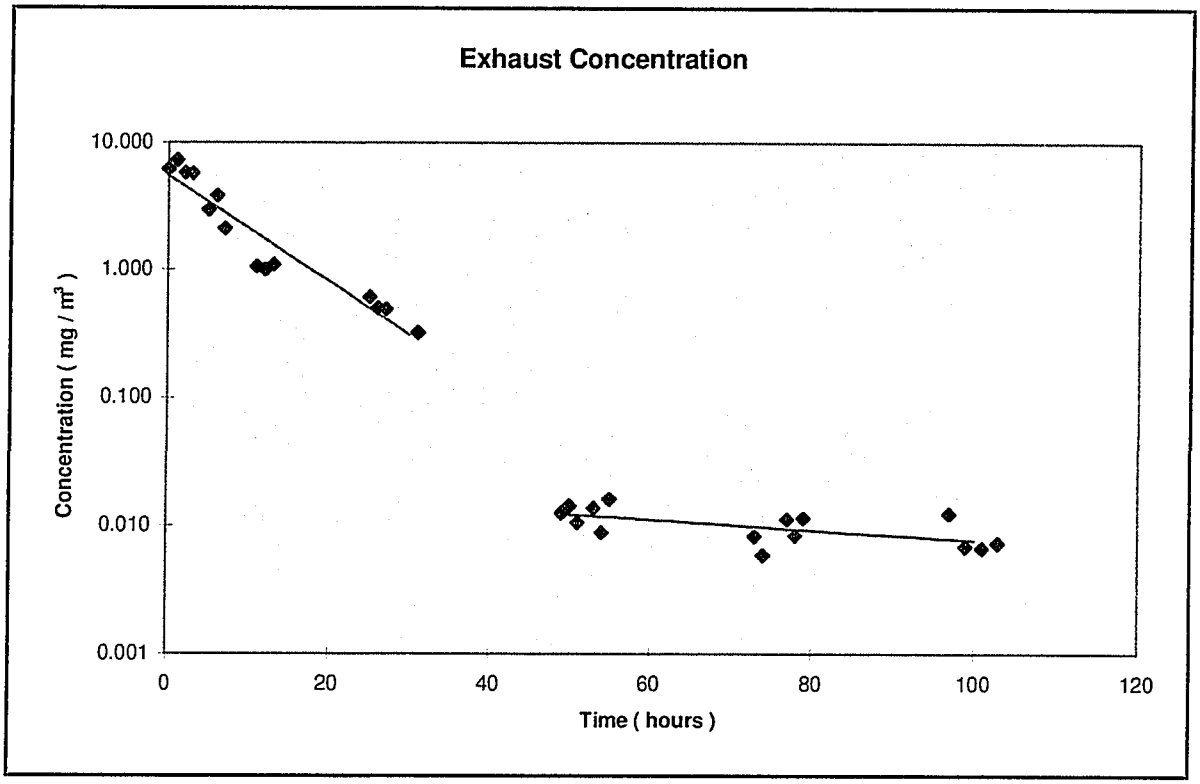


Figure 34 - Concentration of Toluene vs. Time in an Organic Soil (Q_{air} = 3.36 L/h)

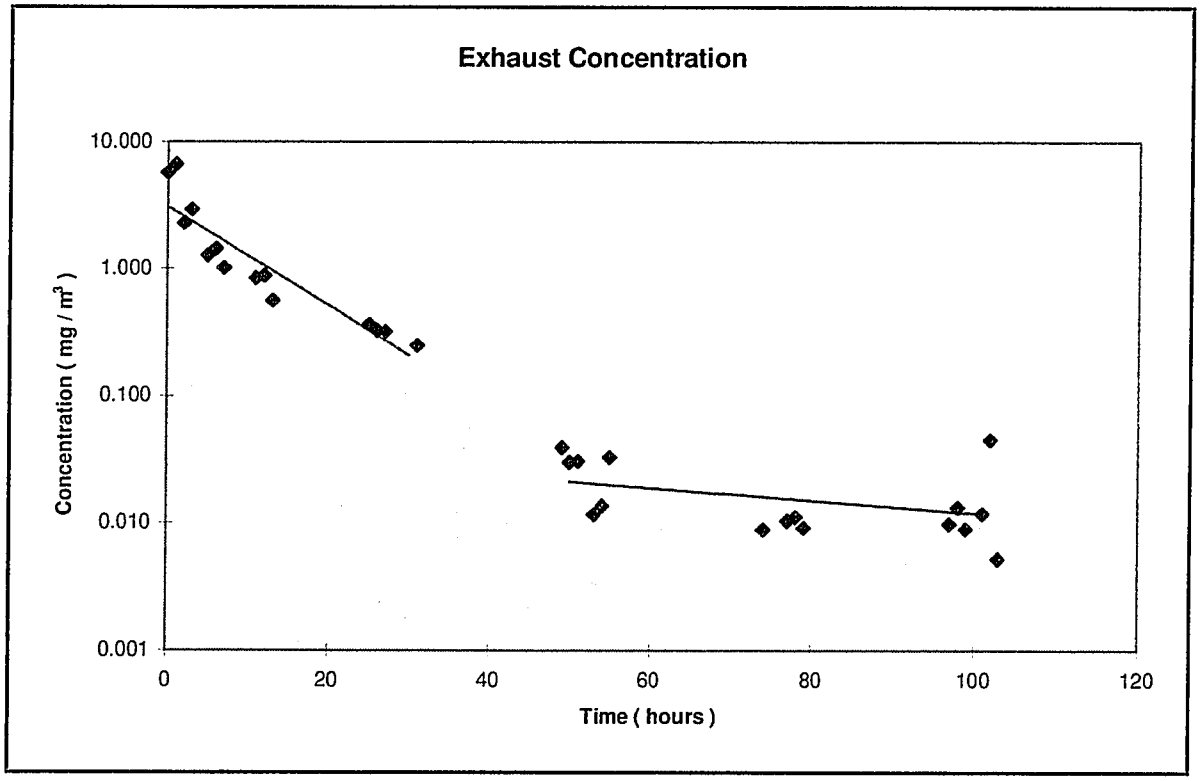


Figure 35 - Concentration of Toluene vs. Time in an Organic Soil (Q_{air} = 7.23 L/h)

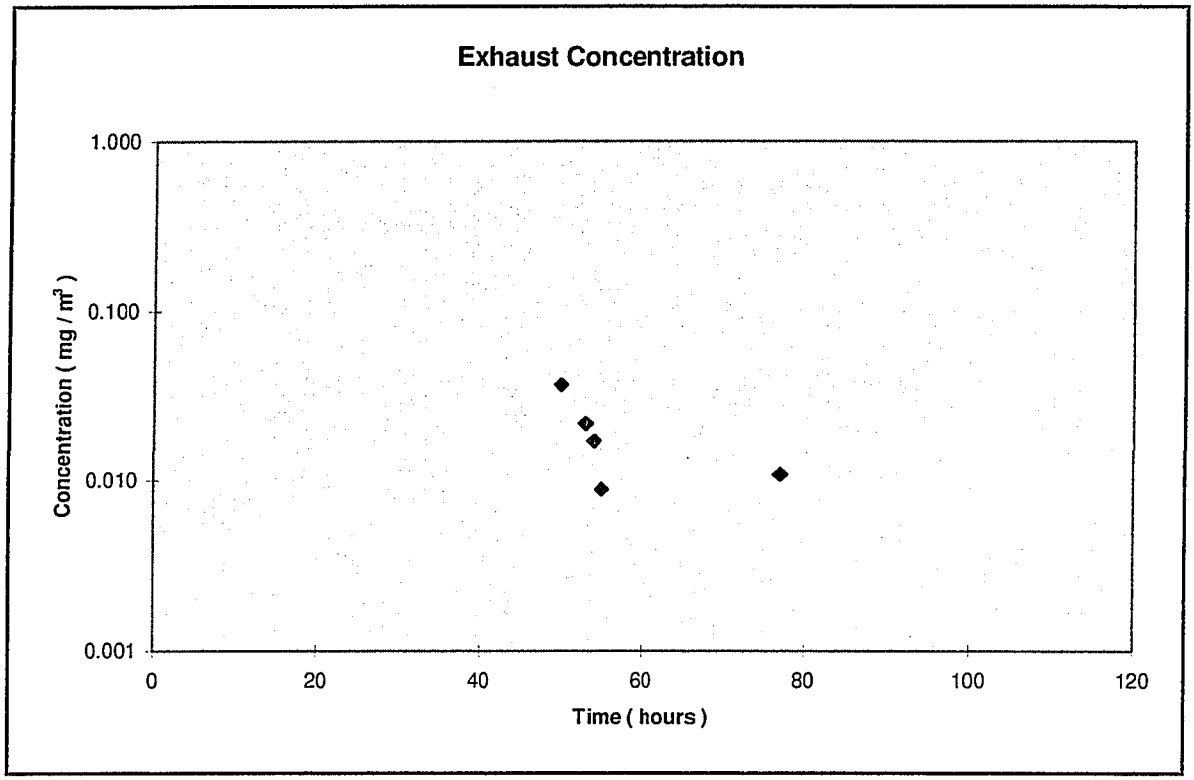


Figure 36 - Concentration of Ethylbenzne vs. Time in a Sandy Soil (Q_{air} = 1.64 L/h)

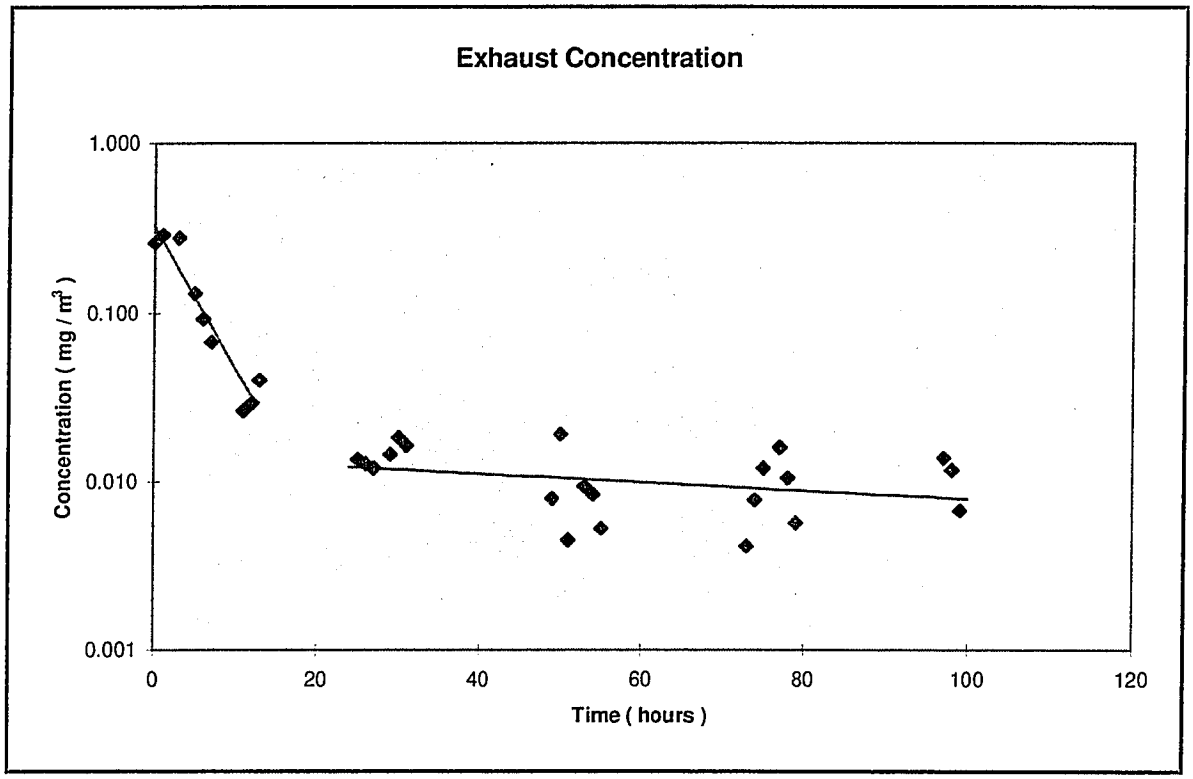


Figure 37 - Concentration of Ethylbenzne vs. Time in a Sandy Soil (Q_{air} = 2.60 L/h)

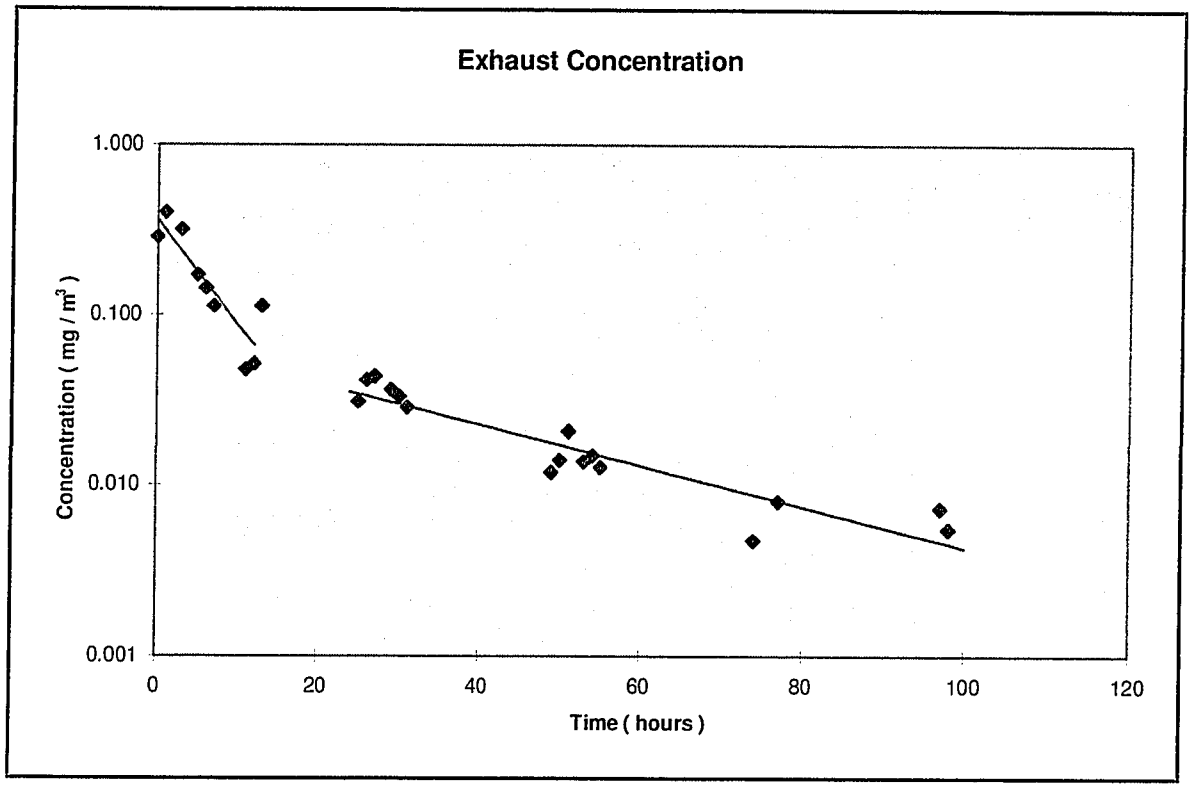


Figure 38 - Concentration of Ethylbenzne vs. Time in a Sandy Soil (Q_{air} = 5.27 L/h)

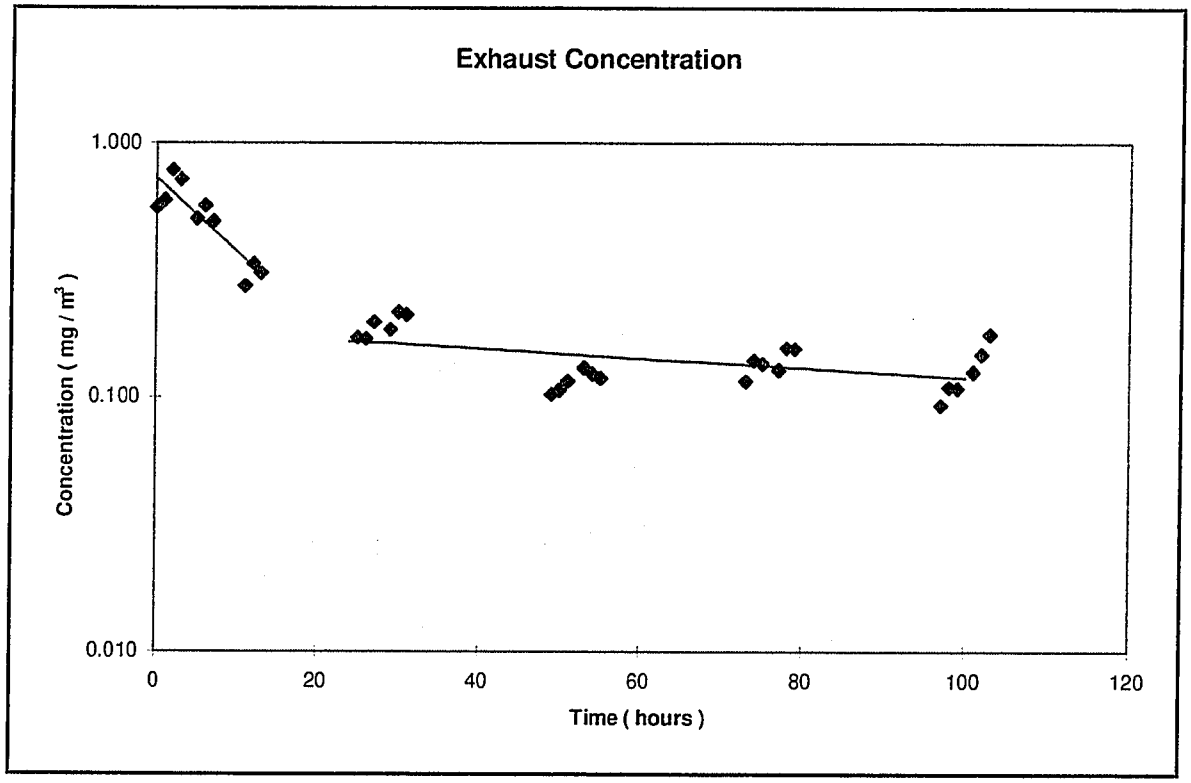


Figure 39 - Concentration of Xylene vs. Time in a Sandy Soil (Q_{air} = 1.46 L/h)

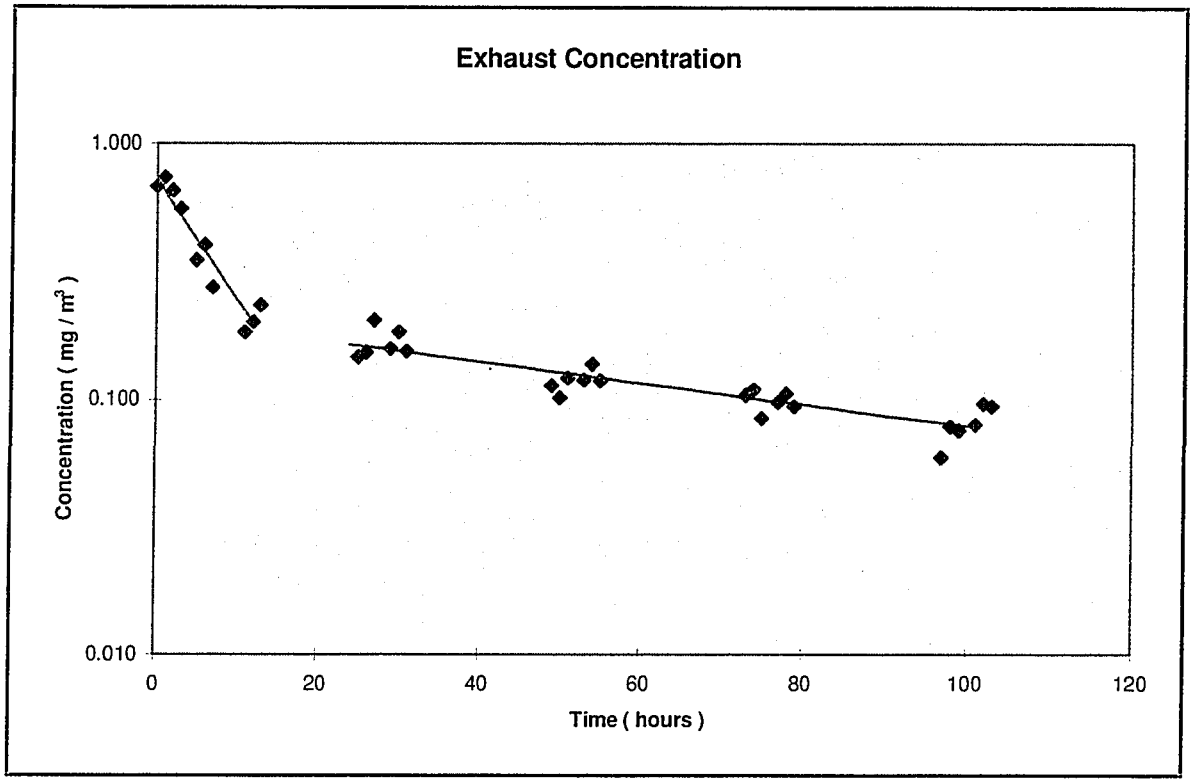


Figure 40 - Concentration of Xylene vs. Time in a Sandy Soil (Q_{air} = 2.89 L/h)

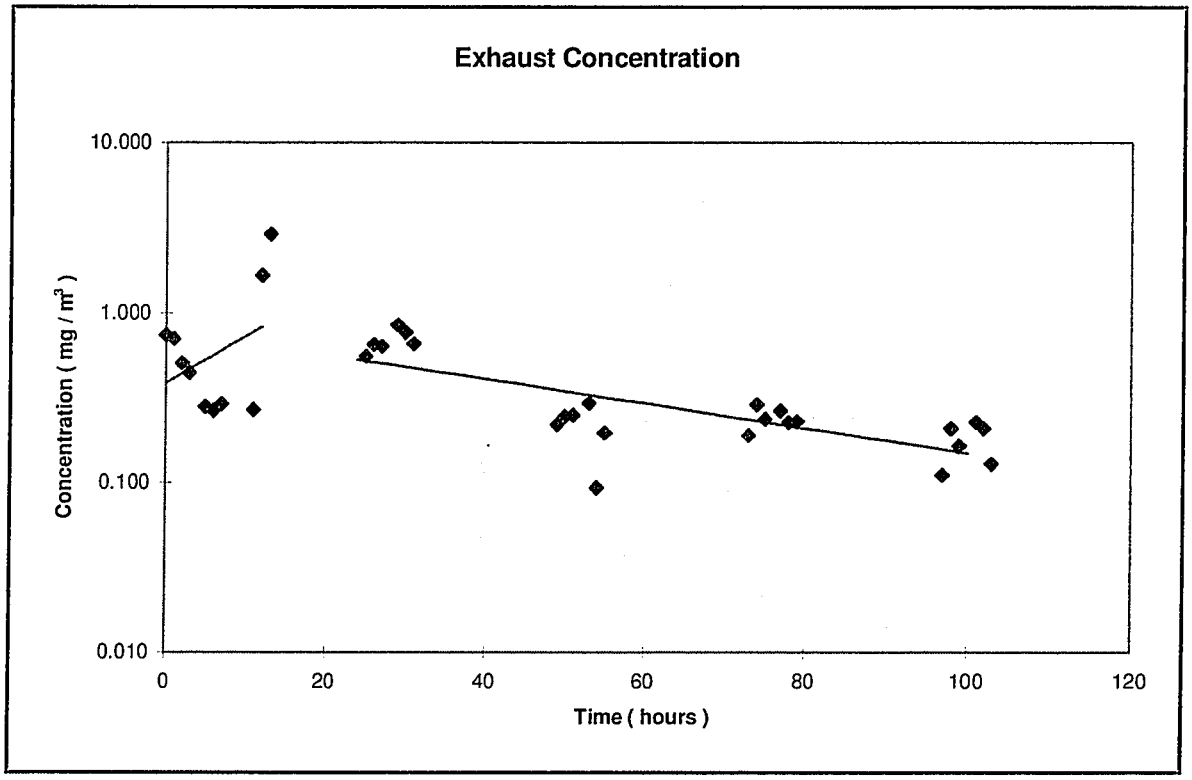


Figure 41 - Concentration of Xylene vs. Time in a Sandy Soil (Q_{air} = 5.55 L/h)

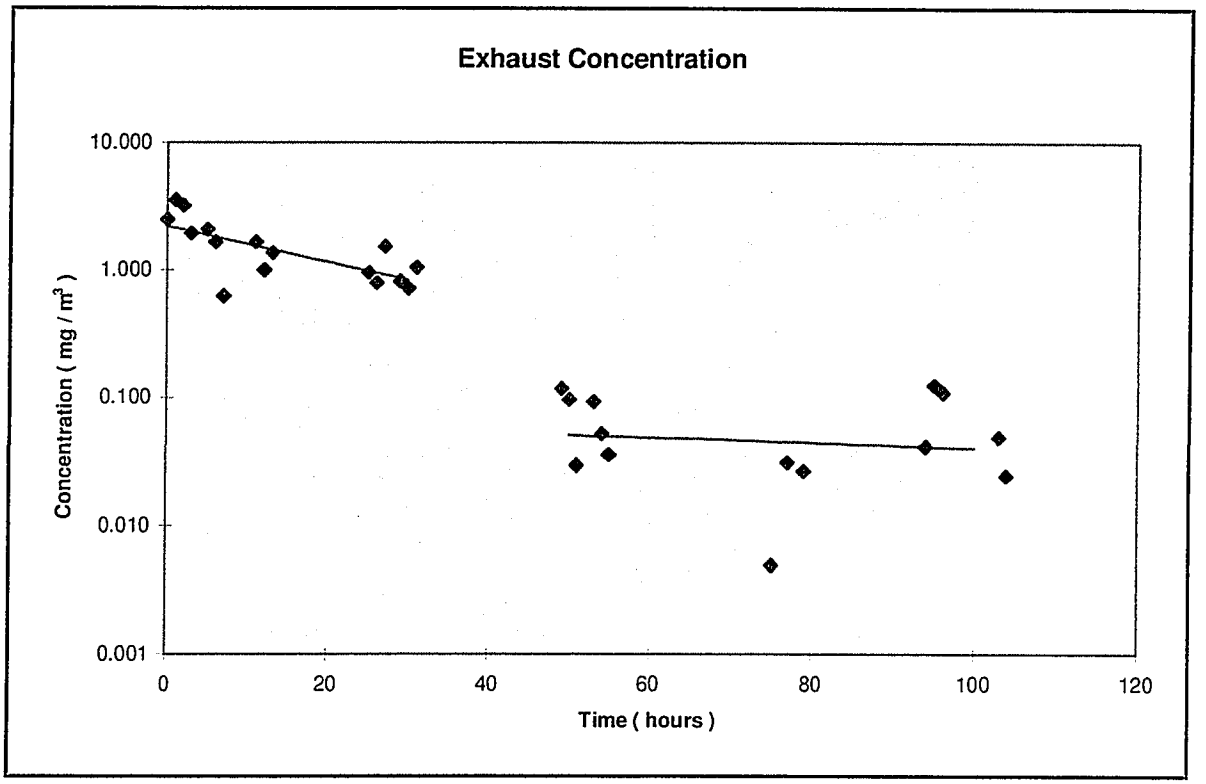


Figure 42 - Concentration of Xylene vs. Time in an Organic Soil (Q_{air} = 1.53 L/h)

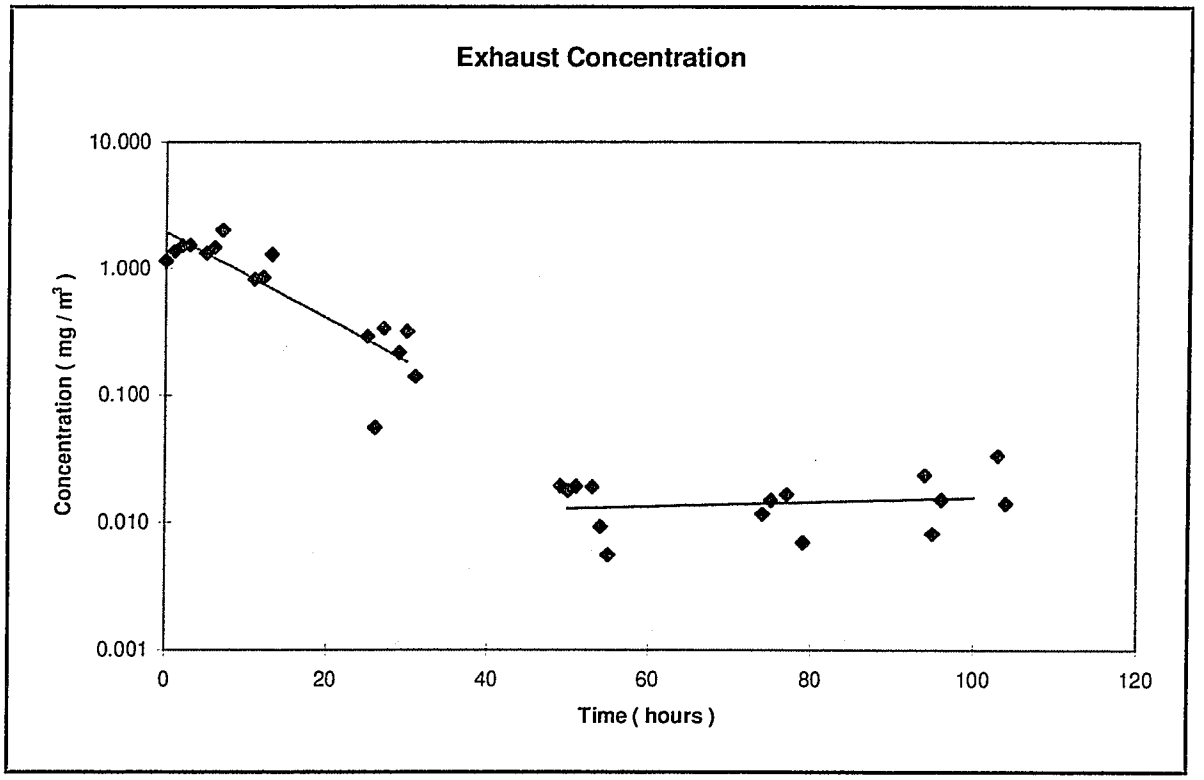


Figure 43 - Concentration of Xylene vs. Time in an Organic Soil (Q_{air} = 3.04 L/h)

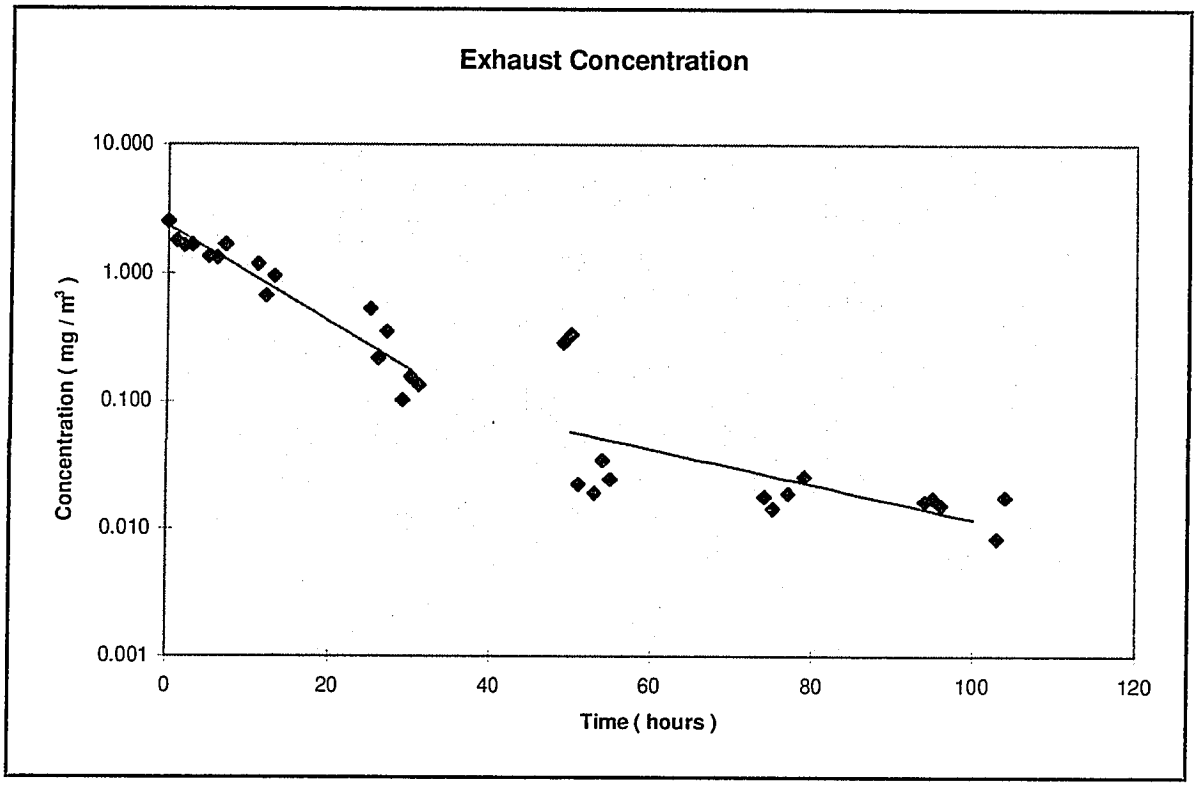


Figure 44 - Concentration of Xylene vs. Time in an Organic Soil (Q_{air} = 5.46 L/h)

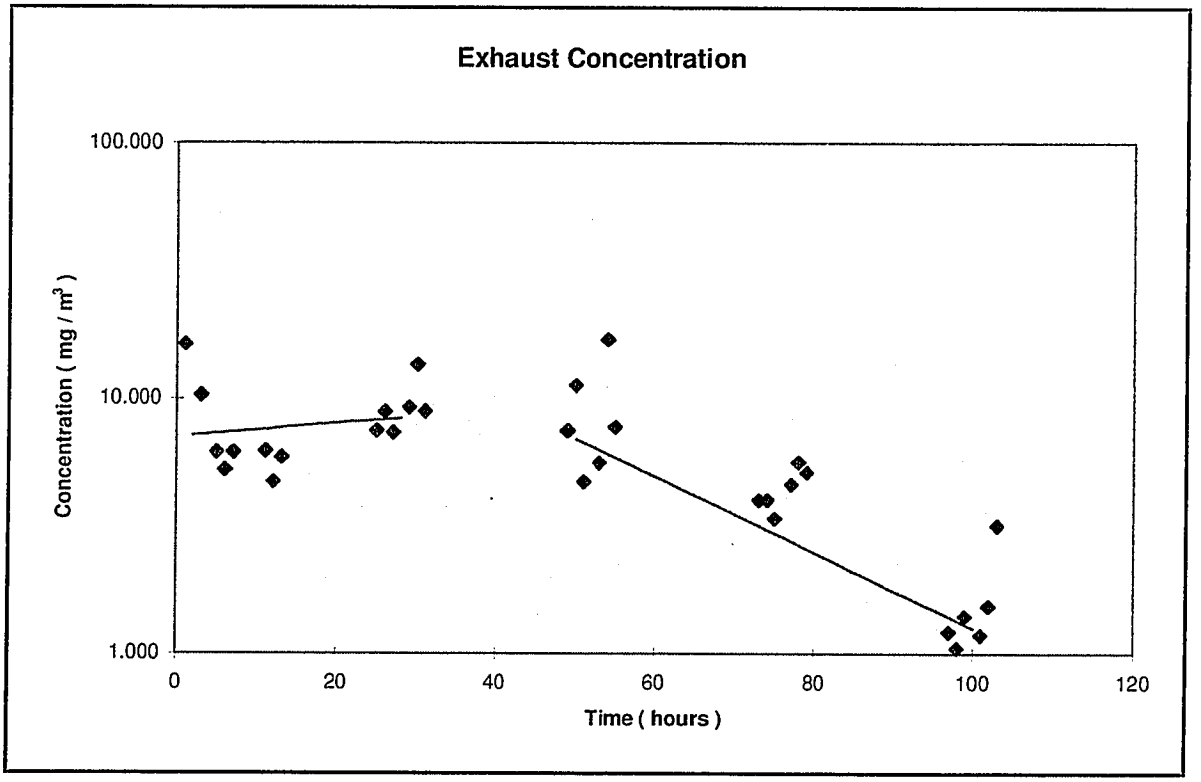


Figure 45 - Concentration of Benzene (in BTEX) in a Sandy Soil (Q_{air} = 1.58 L/h)

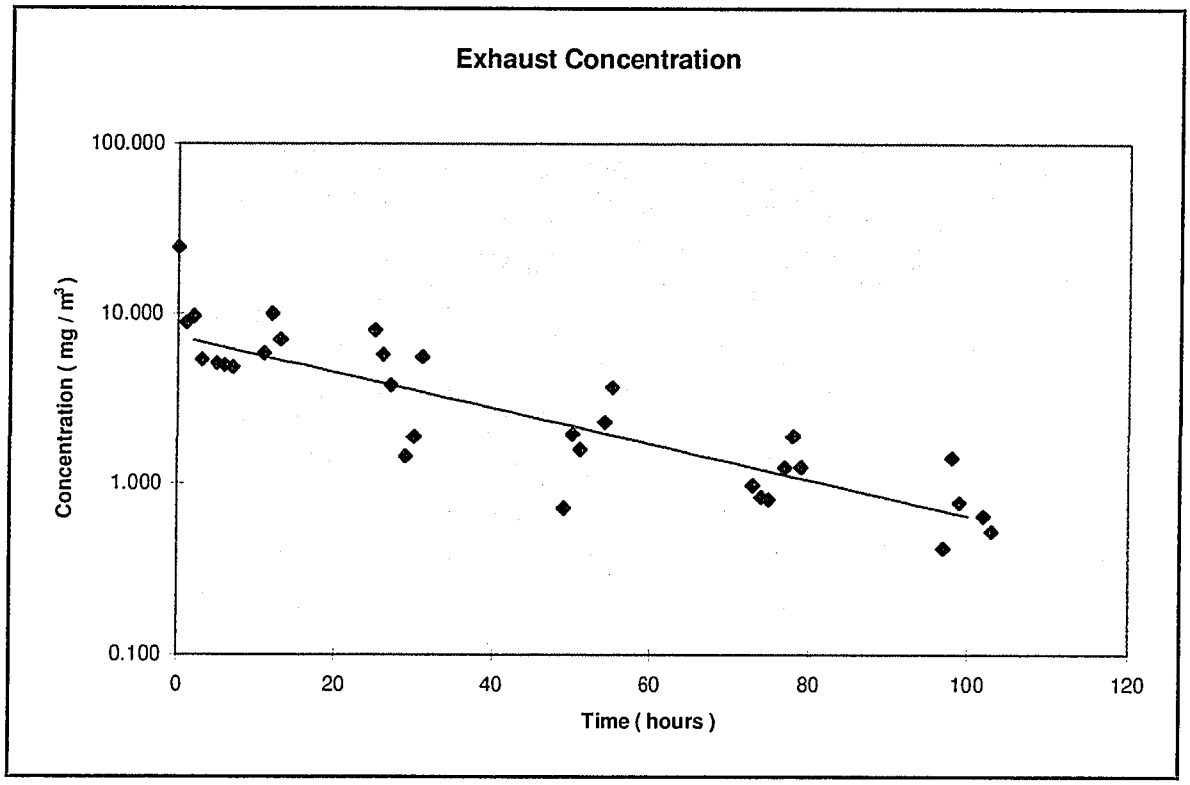


Figure 46 - Concentration of Benzene (in BTEX) in a Sandy Soil (Q_{air} = 3.51 L/h)

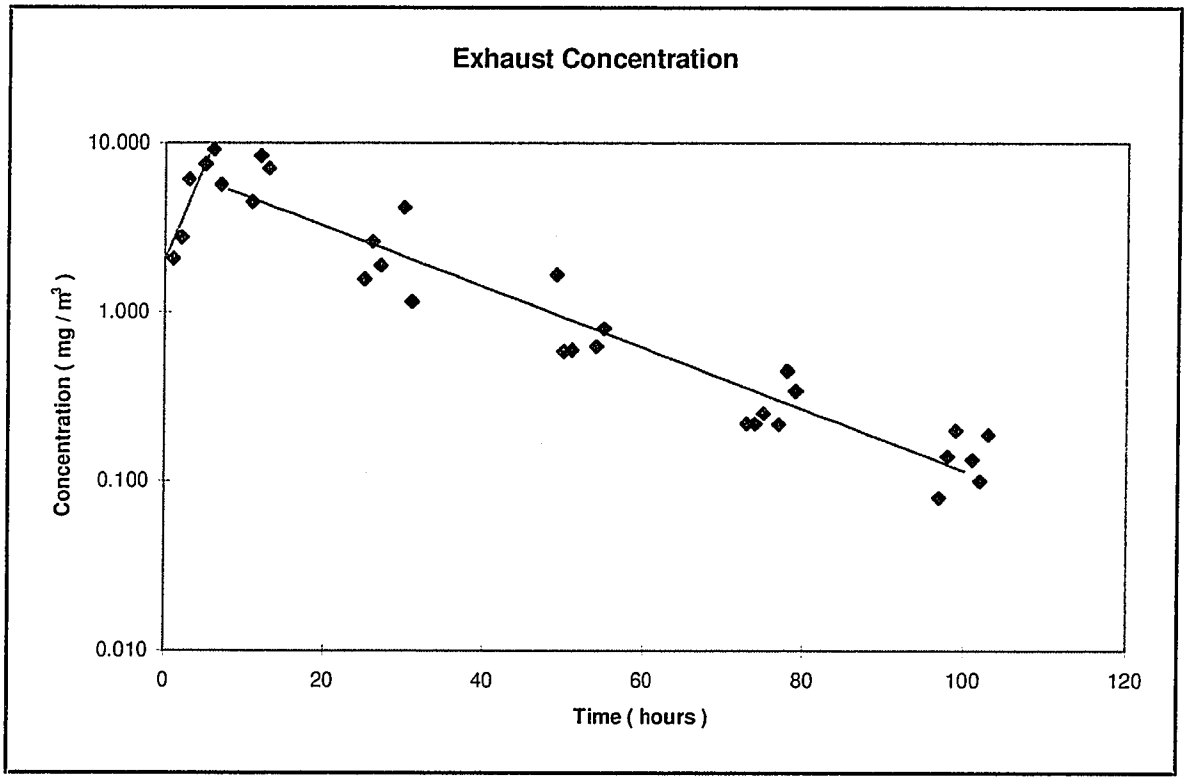


Figure 47 - Concentration of Benzene (in BTEX) in a Sandy Soil (Q_{air} = 5.64 L/h)

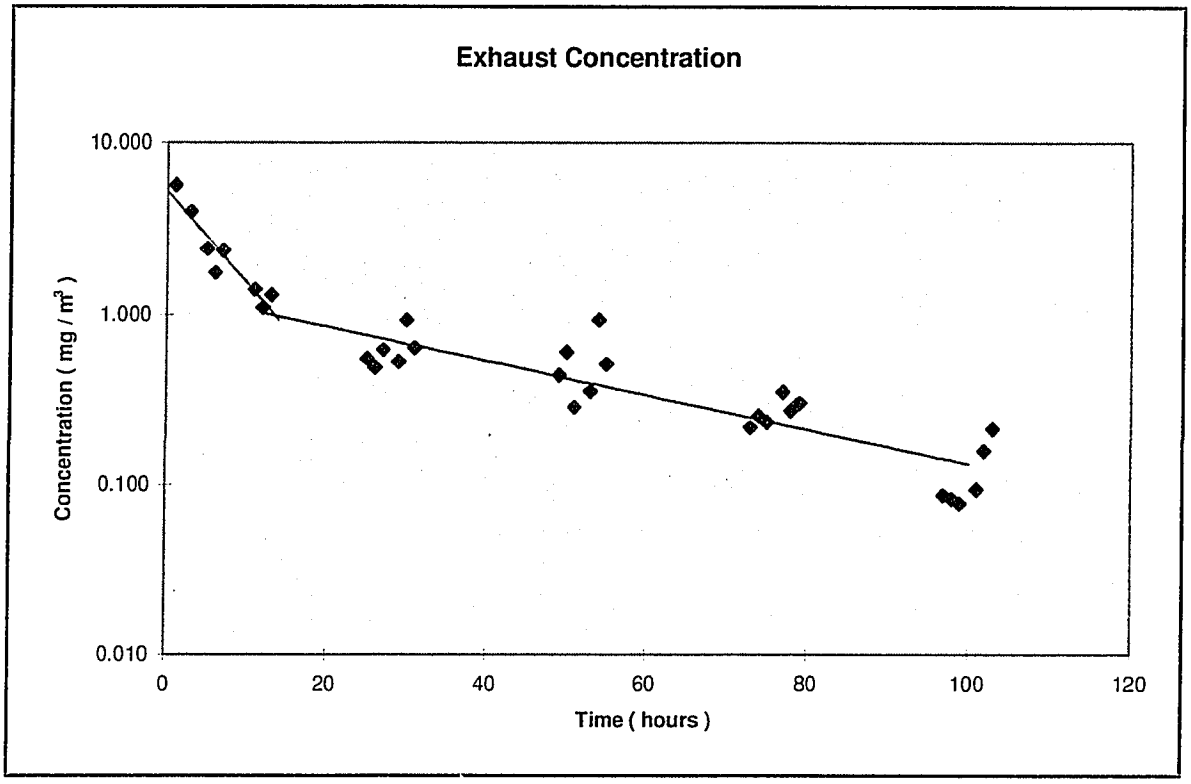


Figure 48 - Concentration of Toluene (in BTEX) in a Sandy Soil (Q_{air} = 1.58 L/h)

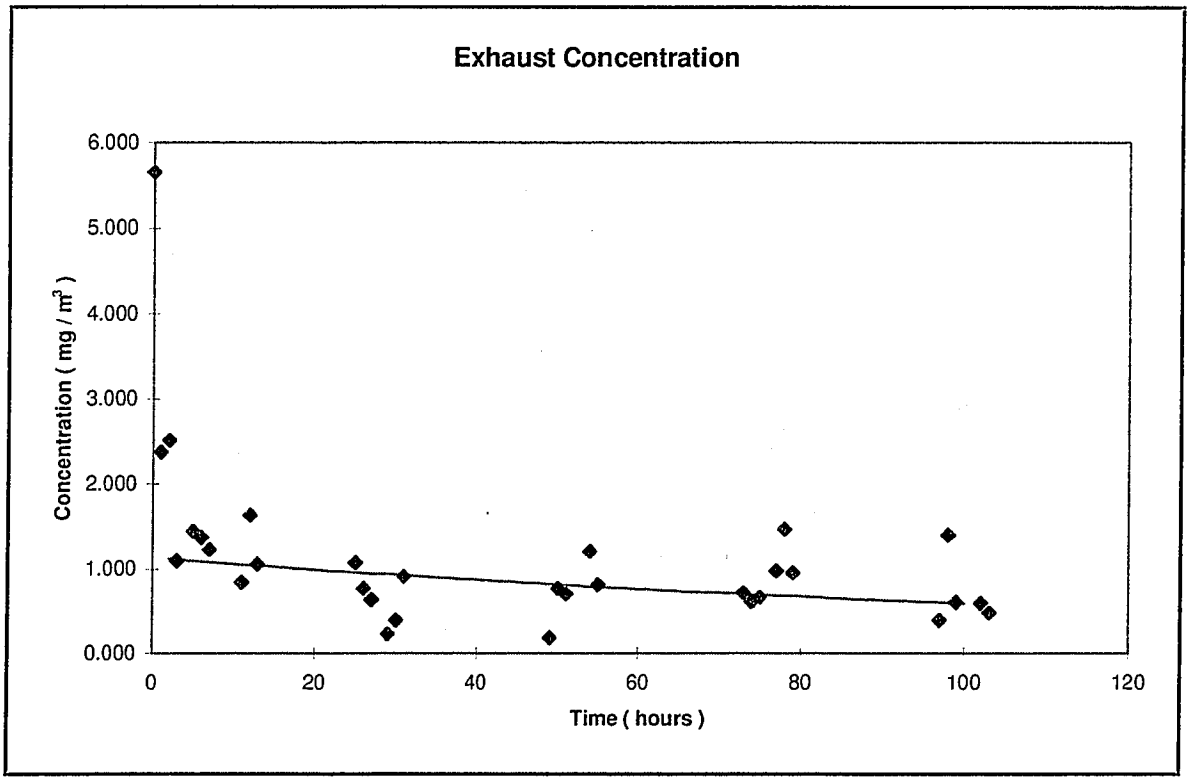


Figure 49 - Concentration of Toluene (in BTEX) in a Sandy Soil (Q_{air} = 3.51 L/h)

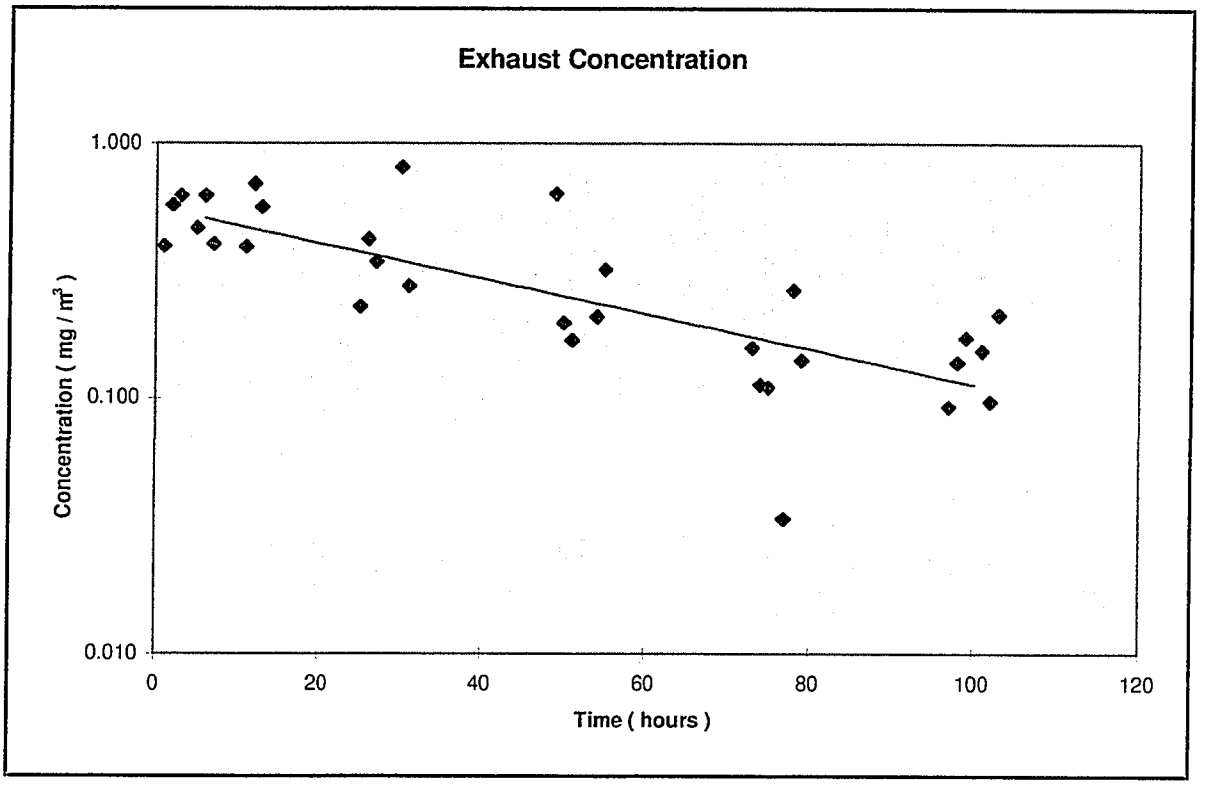


Figure 50 - Concentration of Toluene (in BTEX) in a Sandy Soil (Q_{air} = 5.64 L/h)

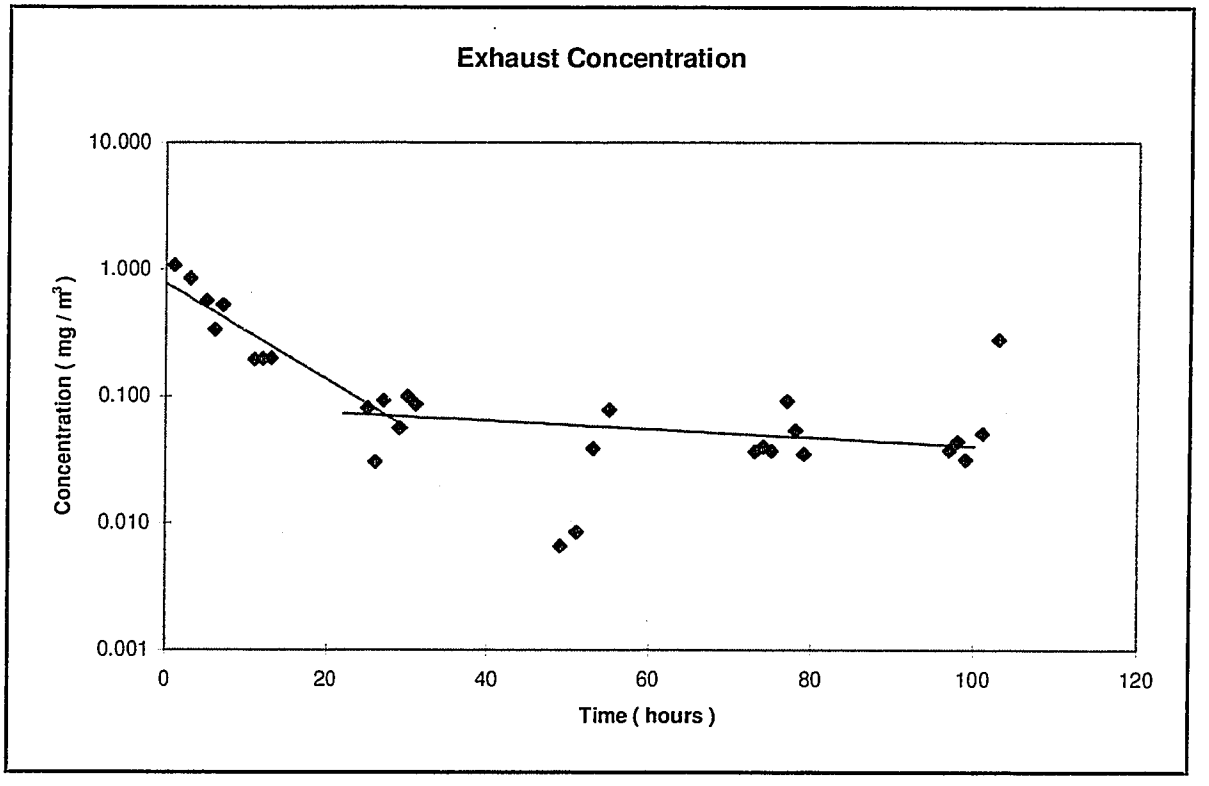


Figure 51 - Concentration of Ethylbenzne (in BTEX) in a Sandy Soil (Q_{air} = 1.58 L/h)

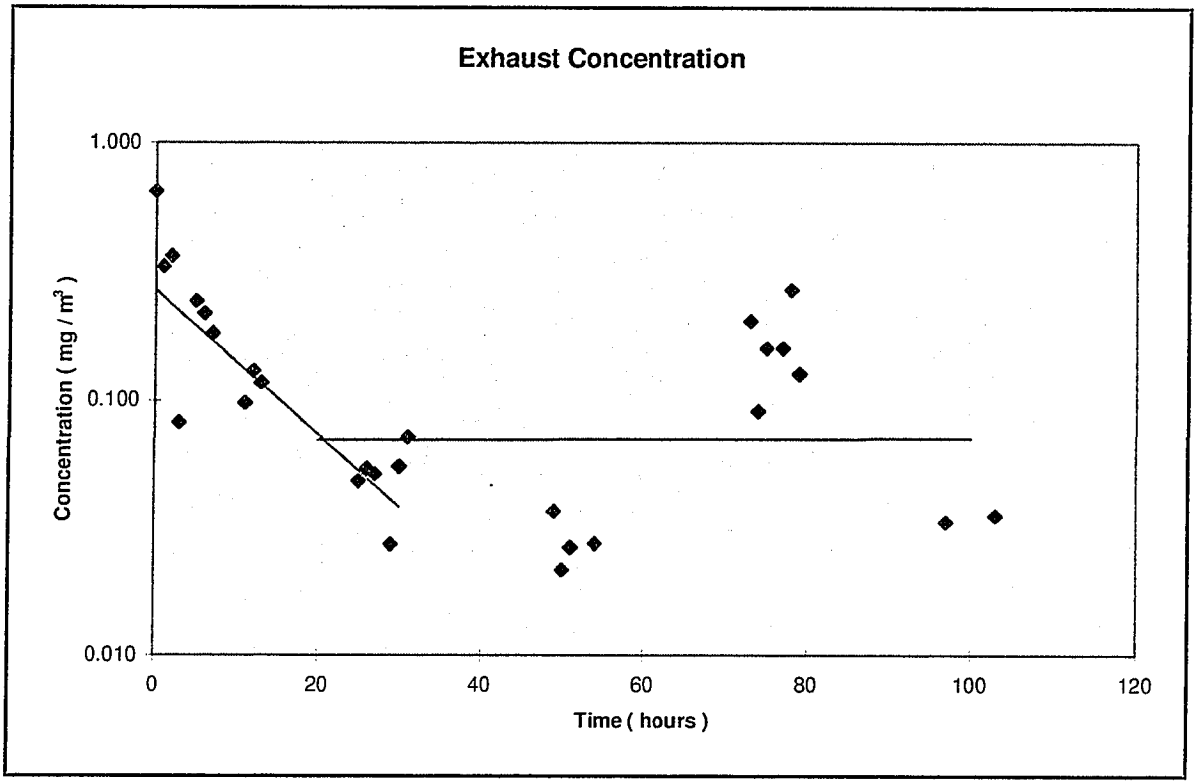


Figure 52 - Concentration of Ethylbenzne (in BTEX) in a Sandy Soil (Q_{air} = 3.51 L/h)

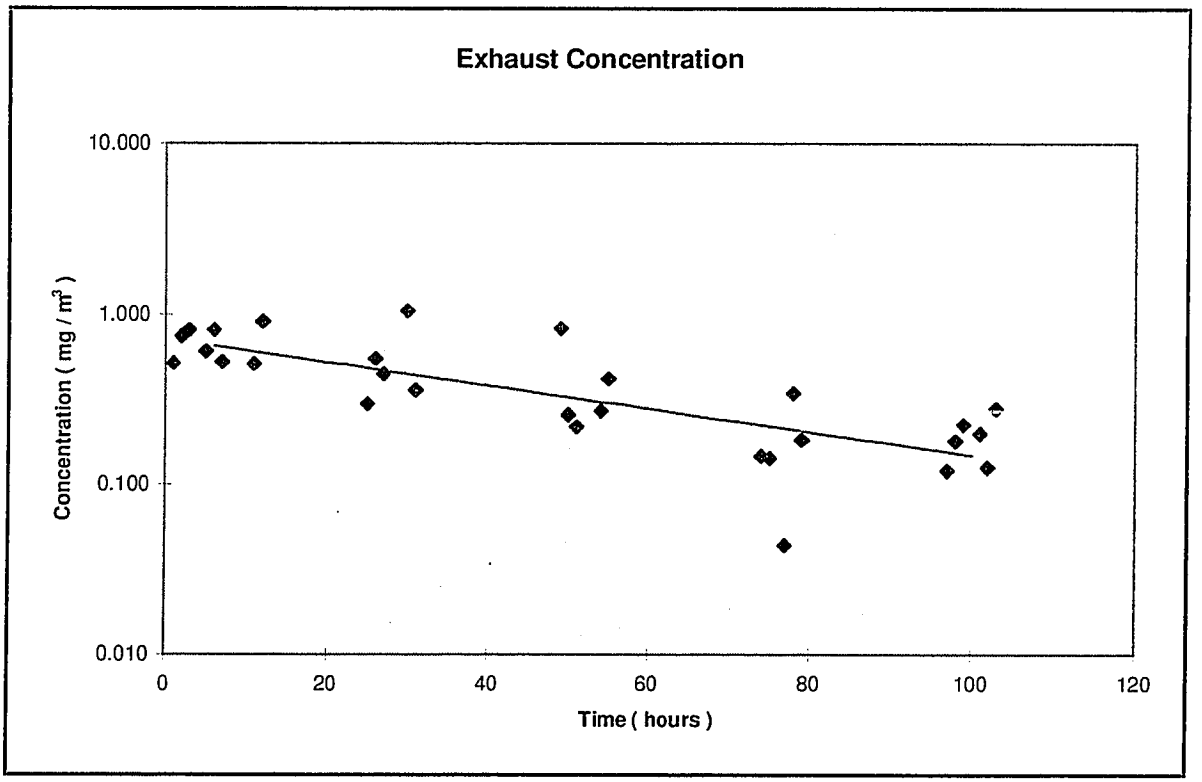


Figure 53 - Concentration of Ethylbenzne (in BTEX) in a Sandy Soil (Q_{air} = 5.64 L/h)

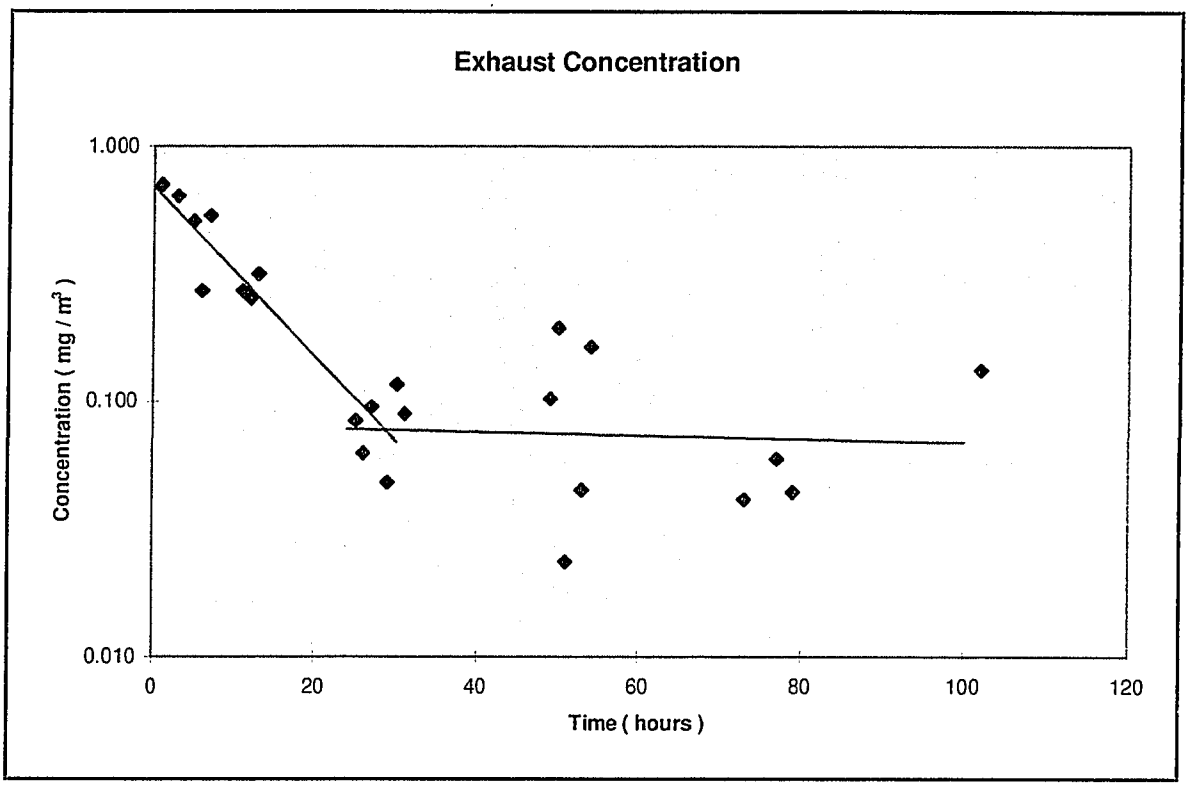


Figure 54 - Concentration of Xylene (in BTEX) in a Sandy Soil (Q_{air} = 1.58 L/h)

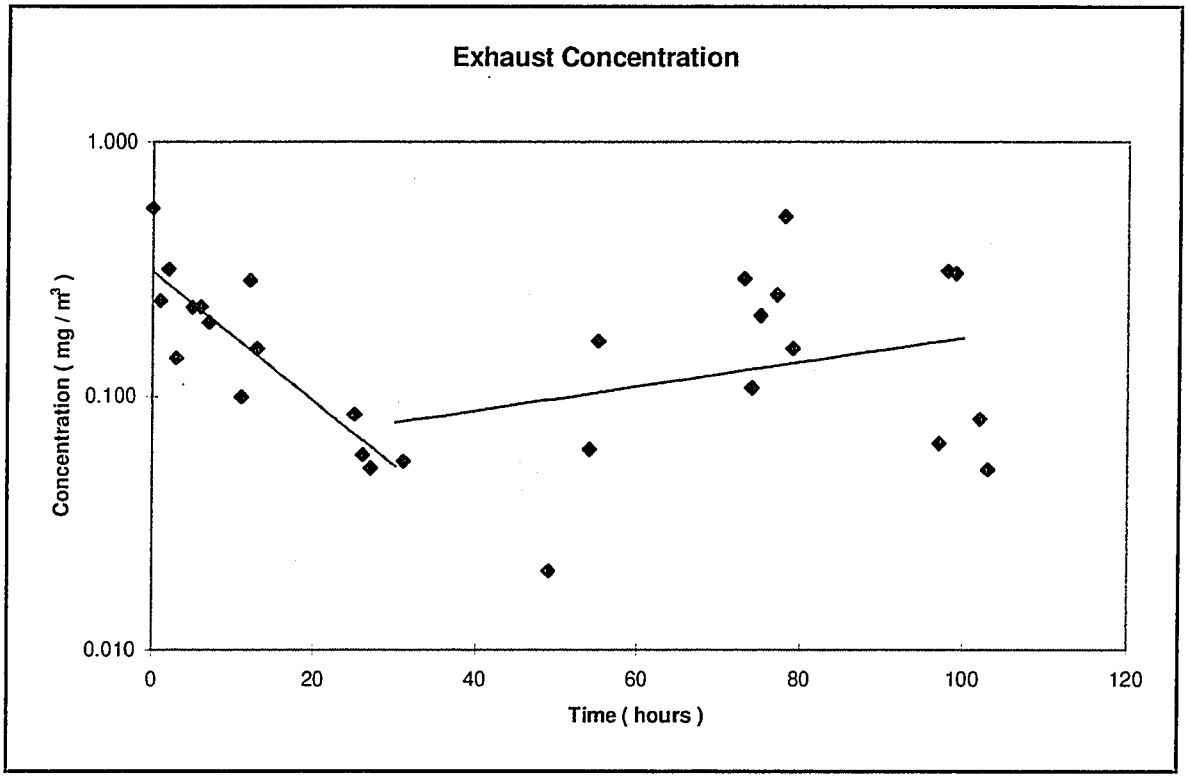


Figure 55 - Concentration of Xylene (in BTEX) in a Sandy Soil (Q_{air} = 3.51 L/h)

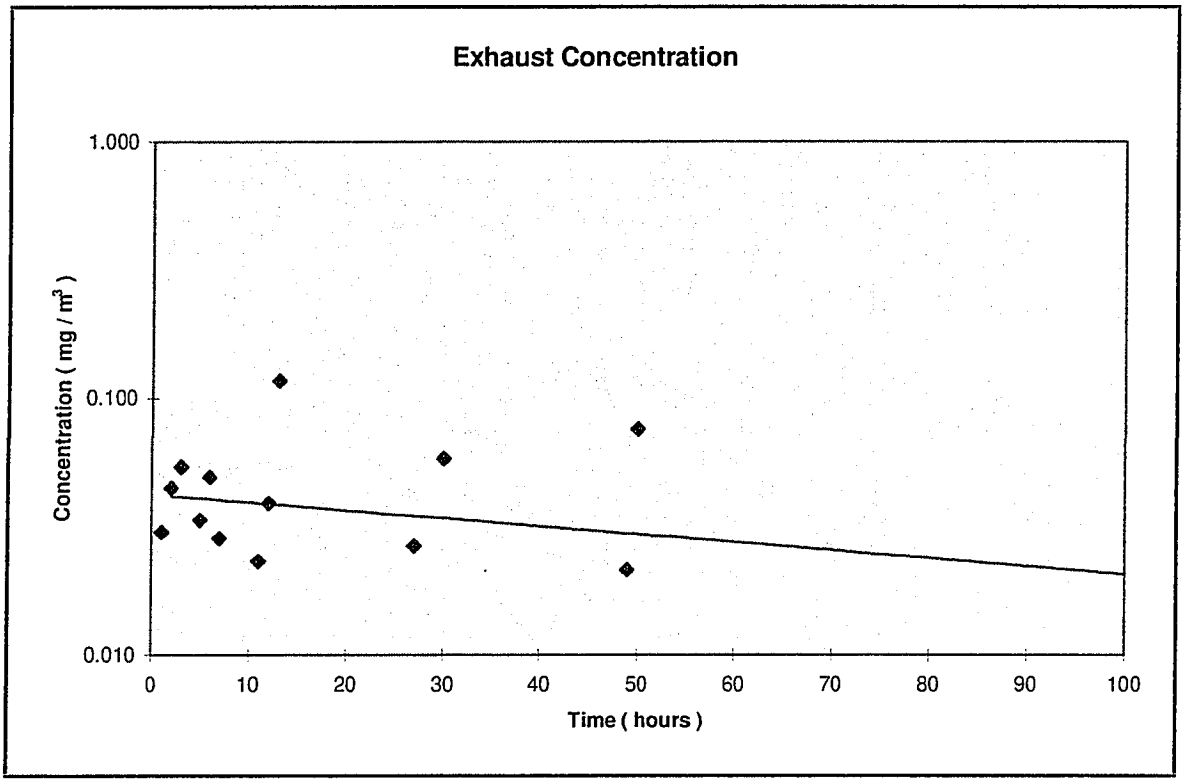


Figure 56 - Concentration of Xylene (in BTEX) in a Sandy Soil (Q_{air} = 5.64 L/h)

5.2.2 Stripping Rate Kinetics

First order curves were fitted to the effluent concentrations vs. time recorded during each experiment. For most experiments three distinctive sections can be seen for each graph: an initial logarithmic part, a transitional section and a final logarithmic section with a gentle slope. Both the initial concentration, C_o, and the exponential decay constant, k, were calculated according to Equation 13. The results are presented in Tables 21 and 22. The corresponding correlation coefficients are presented in Table 23.

The complete sets of data for each experiment are available on the disk enclosed with this thesis. Only the fitted curves are presented here, unless otherwise noted.

$$C = C_o \cdot e^{-kt} \qquad \textbf{Equation 13}$$

C = concentration at time t, mg/L
Co = initial concentration, mg/L
k = exponential decay coefficient, $hours^{-1}$
t = time, hours

Table 21 - Calculated Initial Concentrations in Exhaust Air Streams

INITIAL CONCENTRATION (mg / L)		AIR FLOW RATE L/hr		
COMPOUND	MEDIA	LOW (Apr. 1.5)	MEDIUM (Apr. 3.0)	HIGH (Apr. 6.0)
Benzene	Sand	1.163,13.615	23.969,0.672	7.279,0.597
Toluene	Sand	1.374,0.033	0.611,0.012	0.679,0.017
Ethylbenzene	Sand	n / a	0.325,0.014	0.363,0.068
Xylene	Sand	0.728,0.183	0.723,0.208	0.384,0.792
Benzene	Organic	7.053,0.005	4.359,0.012	6.364,0.030
Toluene	Organic	7.114,0.009	5.499,0.019	3.115,0.037
Xylene	Organic	2.224,0.064	1.958,0.011	2.354,0.281
Mixture of all BTEX Compounds				
Benzene	Sand	7.100,38.502	7.295	2.054,7.422
Toluene	Sand	5.281,1.346	1.130	0.560
Ethylbenzene	Sand	0.782,0.088	0.270,0.070	0.718
Xylene	Sand	0.697,0.081	0.311,0.057	0.042
Saturated Air Used for Stripping				
Toluene	Sand	0.299,0.008	0.432,0.575	0.011,0.285

The explanation for the exhaust concentration curves to, for most of the experiments conducted, exhibit three distinctive sections many indicate two separate mass transfer processes taking place. In the initial section we see relatively high concentrations in the exhaust air. The reason for this is that the air stream is in direct contact with water containing the dissolved contaminants. Mass transfer is primarily occurring across the

liquid-air boundary. The transition zone, between the two logarithmic sections, occurs as the dissolved contaminants in direct contact with the air stream are mostly depleted and a second mechanism becomes dominant. In the third zone a second logarithmic trend can be seen and is indicative of this second mass transfer process. Diffusion of contaminants from areas not in direct contact with the air stream becomes the primary source of mass. Contaminants in liquid pockets, absorbed by soil particles and adsorbed onto mineral surfaces and organic matter are removed during this third phase.

Table 22 - Calculated Exponential Decay Coefficients in Exhaust Air Streams

EXPONENTIAL DECAY COEFFICIENT		AIR FLOW RATE L/hr		
COMPOUND	MEDIA	LOW (Apr. 1.5)	MEDIUM (Apr. 3.0)	HIGH (Apr. 6.0)
Benzene	Sand	-0.292,0.057	0.093,0.034	0.086,0.029
Toluene	Sand	0.079,0.017	0.107,0.005	0.115,0.003
Ethylbenzene	Sand	n / a	0.194,0.006	0.142,0.028
Xylene	Sand	0.067,0.004	0.107,0.010	-0.064,0.017
Benzene	Organic	0.080,0.004	0.103,0.010	0.221,0.031
Toluene	Organic	0.084,0.003	0.096,0.009	0.090,0.011
Xylene	Organic	0.033,0.005	0.079,-0.004	0.086,0.032
Mixture of all BTEX Compounds				
Benzene	Sand	-0.006,0.034	0.024	-0.262,0.042
Toluene	Sand	0.124,0.023	0.007	0.016
Ethylbenzene	Sand	0.088,0.008	0.065,0.000	0.016
Xylene	Sand	0.007,0.002	0.059,0.011	0.007
Saturated Air Used for Stripping				
Toluene	Sand	0.262,0.000	-0.093,0.014	-0.442,0.036

Table 23 - Correlation Coefficients for Fitted Curves

CORRELATION COEFFICIENT		AIR FLOW RATE L/hr		
COMPOUND	MEDIA	LOW (Apr. 1.5)	MEDIUM (Apr. 3.0)	HIGH (Apr. 6.0)
Benzene	Sand	0.974*,0.870*	0.817*,0.942*	0.901*,0.955*
Toluene	Sand	0.951*,0.796*	0.900*,0.988*	0.842*,0.995*
Ethylbenzene	Sand	n/a	0.962*,0.921*	0.863*,0.902*
Xylene	Sand	0.988*,0.994*	0.987*,0.984*	0.947*,0.964*
Benzene	Organic	0.975*,0.969*	0.841*,0.971*	0.690*,0.933*
Toluene	Organic	0.993*,0.987*	0.948*,0.991*	0.908*,0.988*
Xylene	Organic	0.970*,0.904*	0.932*,0.959*	0.935*,0.967*
Mixture of all BTEX Compounds				
Benzene	Sand	0.983*,0.903*	0.857*	0.988*,0.876*
Toluene	Sand	0.974*,0.935*	0.387*	0.775*
Ethylbenzene	Sand	0.913*,0.875*	0.949*,0.952*	0.744*
Xylene	Sand	0.950*,0.958*	0.931*,0.916*	0.117***
Saturated Air Used for Stripping				
Toluene	Sand	0.935*,0.964*	0.956*,0.992*	0.983*,0.919*

* level of significance greater than 0.01
** level of significance greater than 0.05
*** level of significance less than 0.10

It was expected that the initial concentrations in air would be highest for the low flow rate and lowest for the high flow rate. This trend was clearly seen in the experiment conducted using a mixture of all the BTEX components but in the other experiments the trend, was not as clear but did exist. Since the initial concentrations changed with air flow rate, a local equilibrium did not exist.

The decay coefficients show a trend of an increase with an increase in air flow rate and chemical volatility. When in a mixture, the decay coefficient, for all four compounds studied, is much less than when single compounds were stripped. Using saturated air resulted in lower coefficients than seen when dry air was used. Higher coefficients are indicative of greater mass flow rates

5.2.3 Mass Removal Rates

Both the typical plots of contaminant concentration versus time and rate kinetic equation (Equation 13) show that the rate of contaminant mass removal, $\Delta(Q_a \bullet C)/\Delta t$, changed with the contaminant concentration at that time. Therefore, the rate of mass removal decreased with time.

The concentrations in the exhaust gas from each of the column experiments was multiplied by the actual average flow rate, Q_a, to determine the mass flow rate of contaminants from the columns. The flow rates were determined by averaging 15 measurements over five days.

5.2.3.1 Stripping of Individual Contaminants

Figures 57-63 show the mass flow rate at each of the three air flow rates, for all twelve experiments.

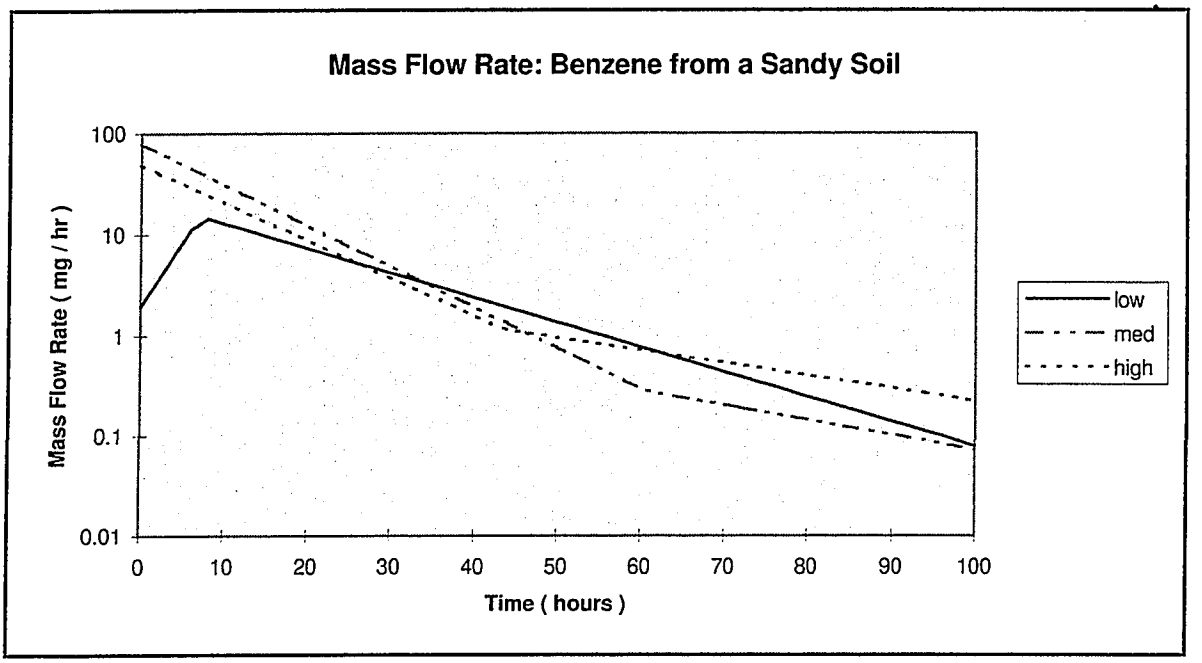


Figure 57 - Mass Flow Rate of Benzene From Sandy Soil

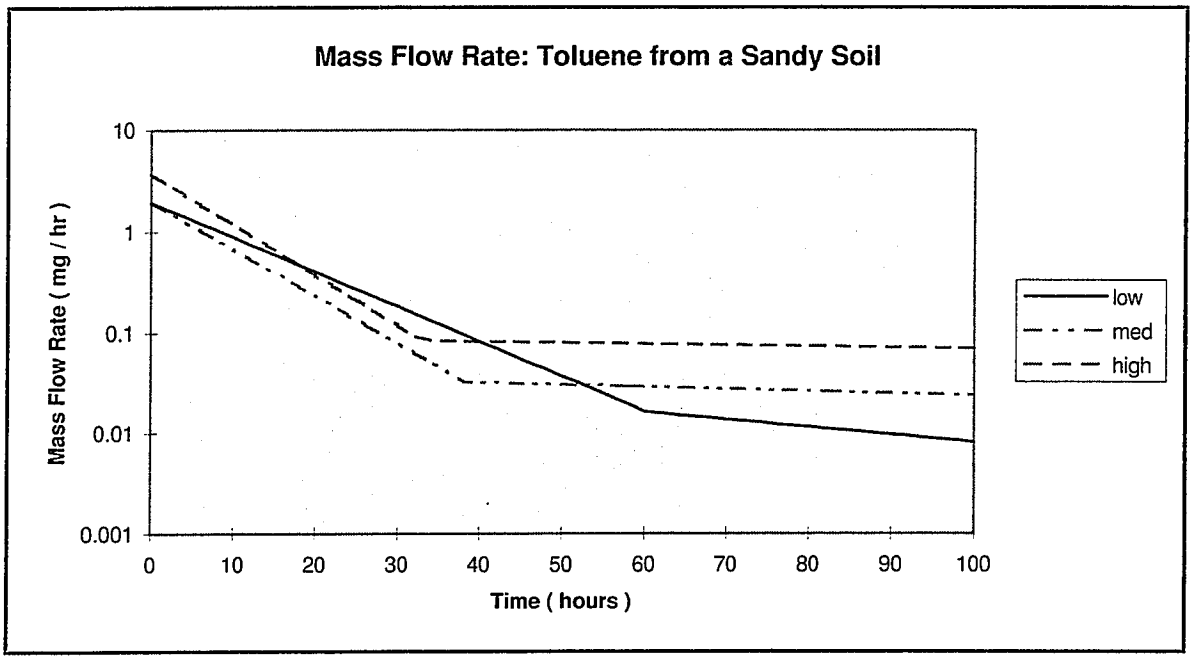


Figure 58 - Mass Flow Rate of Toluene From a Sandy Soil

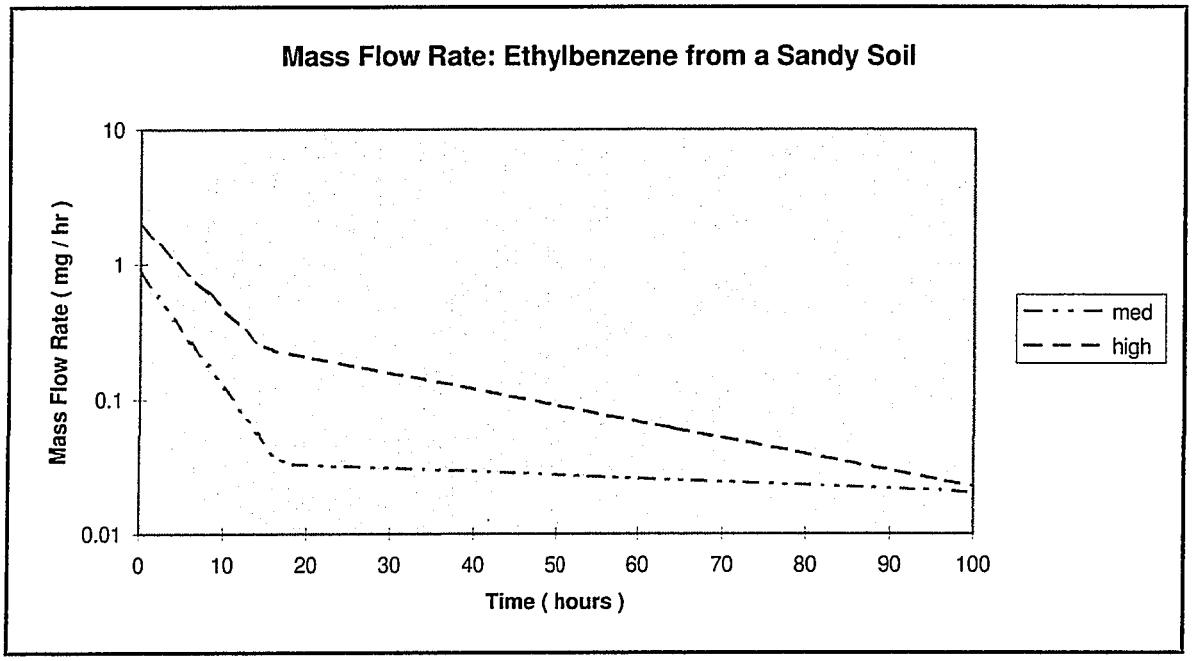


Figure 59 - Mass Flow Rate of Ethylbenzene from a Sandy Soil

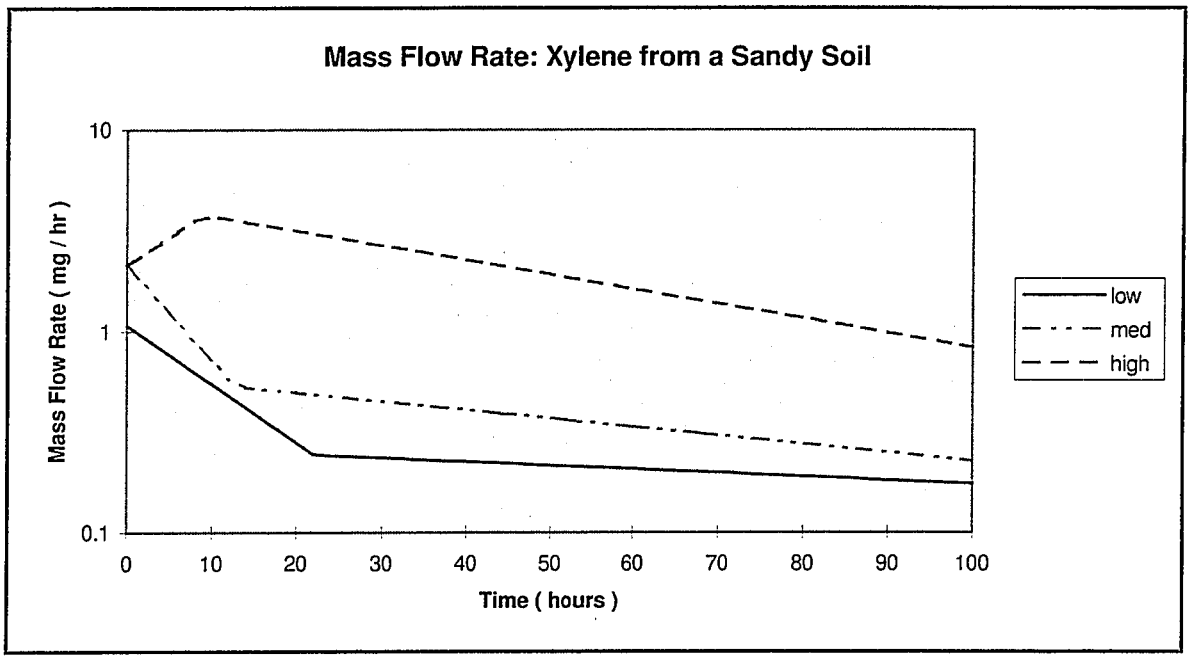


Figure 60 - Mass Flow Rate of Xylene from a Sandy Soil

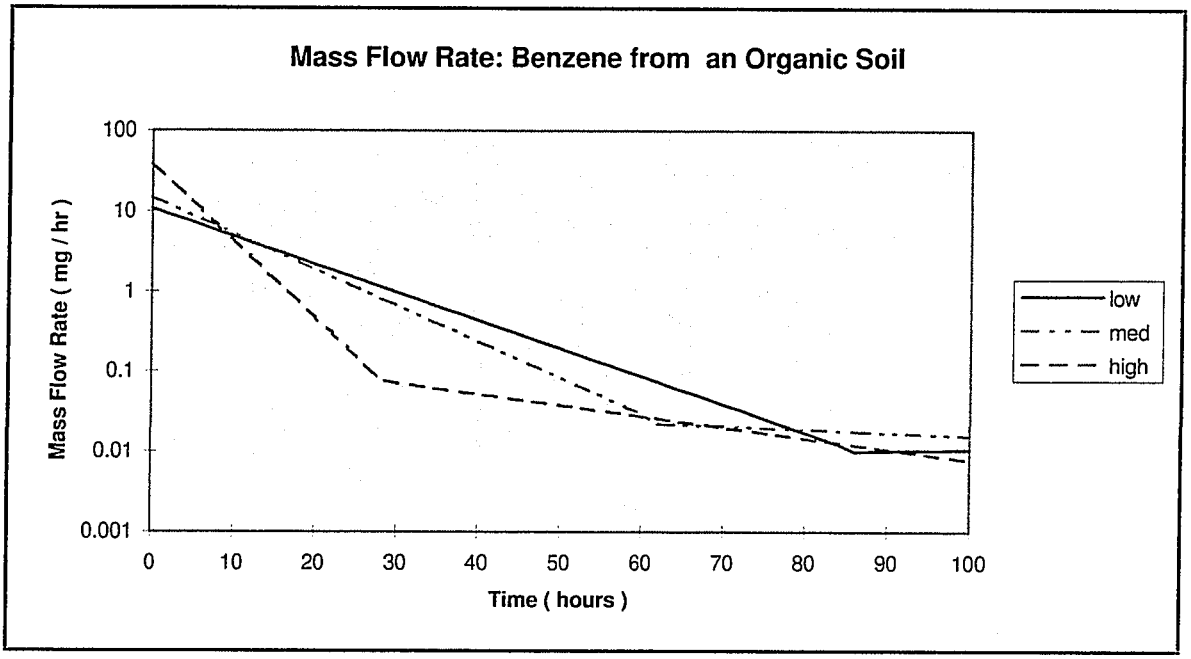


Figure 61 - Mass Flow Rate of Benzene from Organic Soil

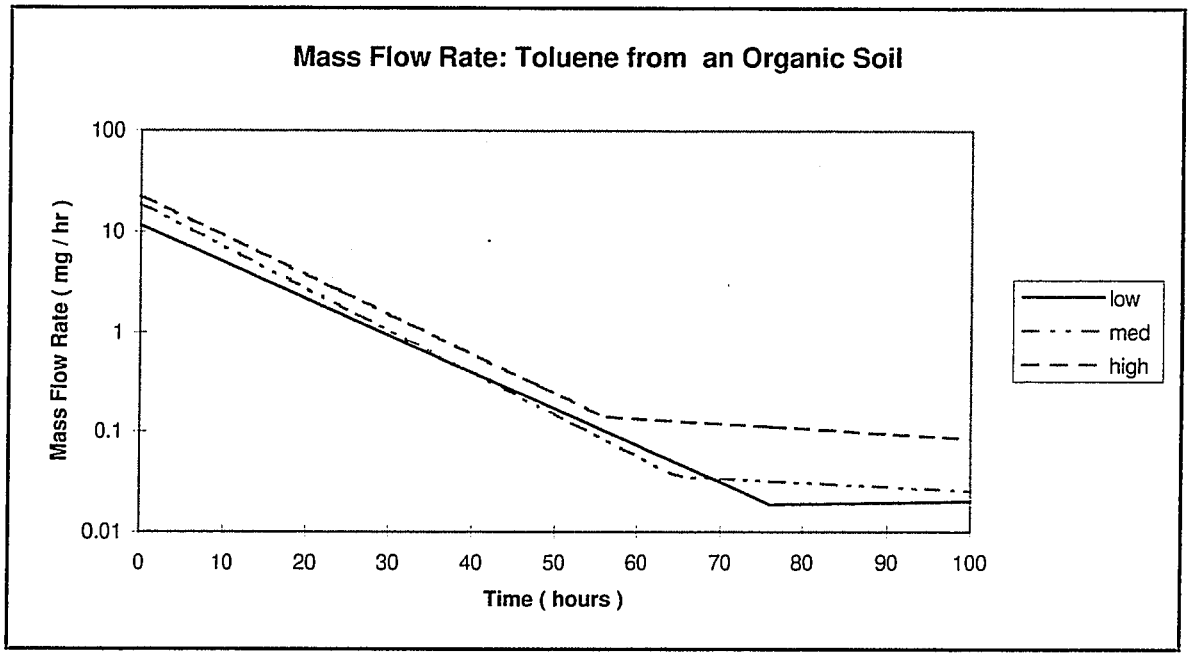


Figure 62 - Mass Flow Rate of Toluene from Organic Soil

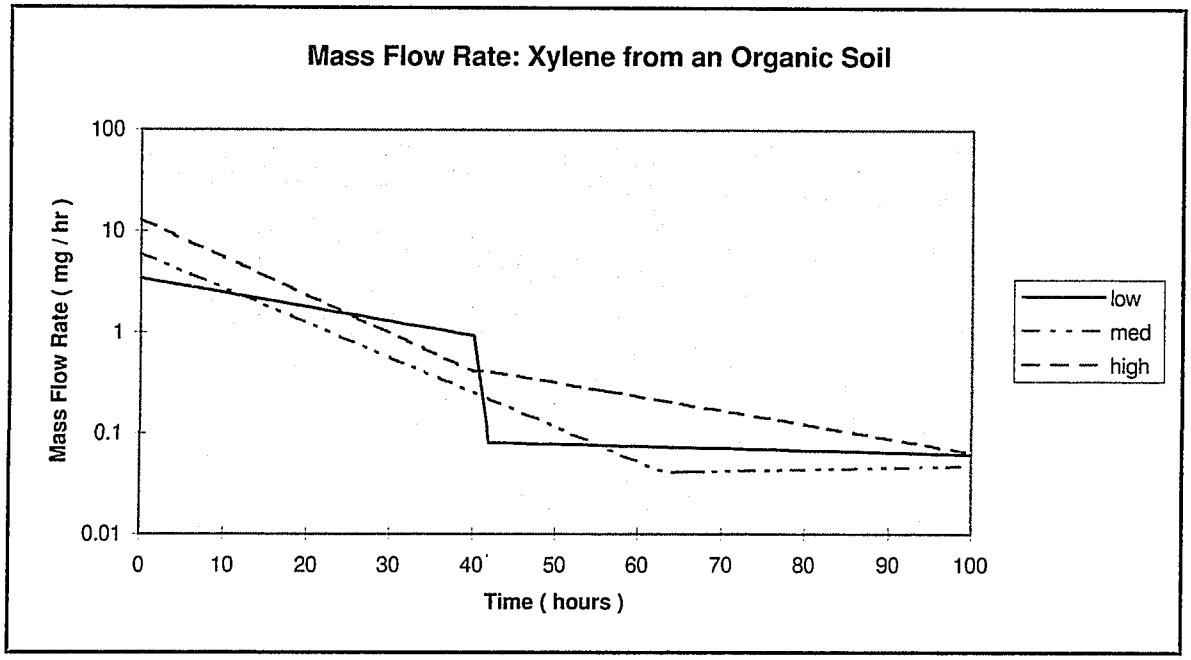


Figure 63 - Mass Flow Rate of Xylene from Organic Soil

The removal rates of all four BTEX compounds, when stripped individually from the sandy soil, showed a decrease in exhaust concentrations as air flow rate was increased. This indicates that the effluent air exiting the columns, at all three flow rates, was not saturated with the contaminants. The equilibrium behaviour that other researchers have seen, when striping gasoline as an NAPL, did not exist under these conditions. If an equilibrium were to exist, a period of constant concentration and mass flow rate would have been seen in the effluent.

The three experiments, run with the organic soil, showed relatively less variations at the three flow rates. This may be an indication that a large amount of the compounds added to the soil initially were sorbed onto the organic matter. It can be concluded that the maximum rate of mass transfer across the water-air interface occurred at the three air flow rates. This indicates that the limiting step was the desorption of the chemicals from

the organic matter into the pore water. At higher air flow rates, the mass flow rates out of the columns were slightly higher, which can be attributed to higher turbulence, resulting in better mixing.

5.2.3.2 Stripping of Contaminant Mixture

Figures 64 to 67 show the corresponding mass flow rates versus time, at different air flow rates for BTEX stripped from sandy soil as a mixture.

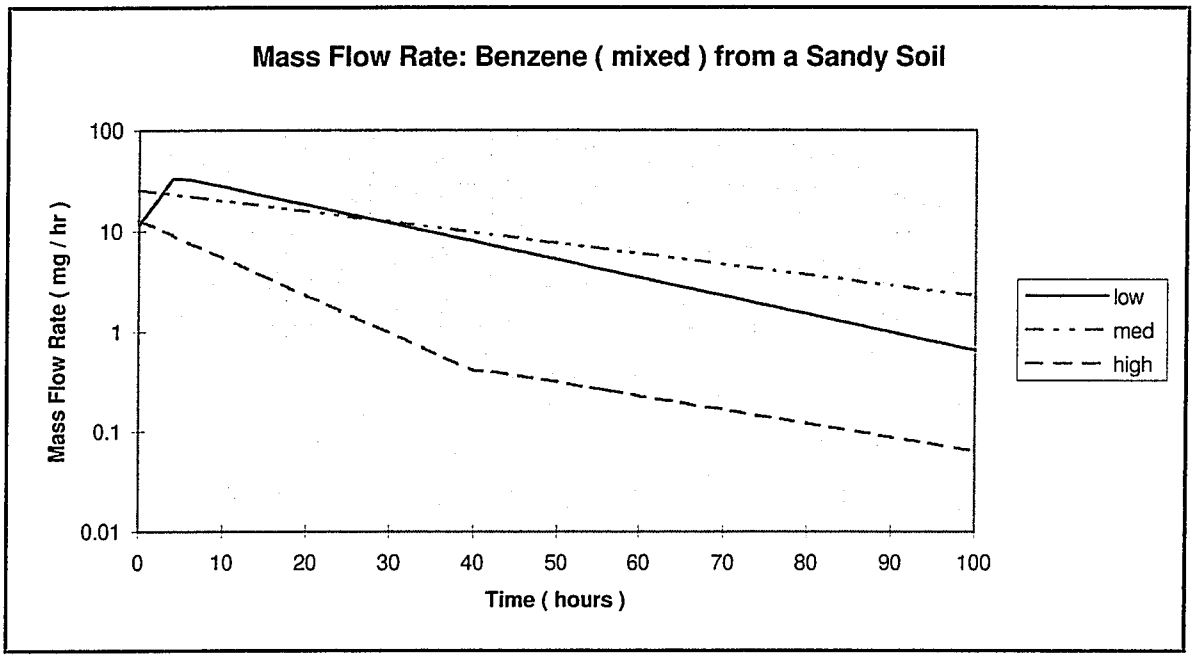


Figure 64 - Mass Flow Rate of Benzene from a BTEX mixture in Sandy Soil

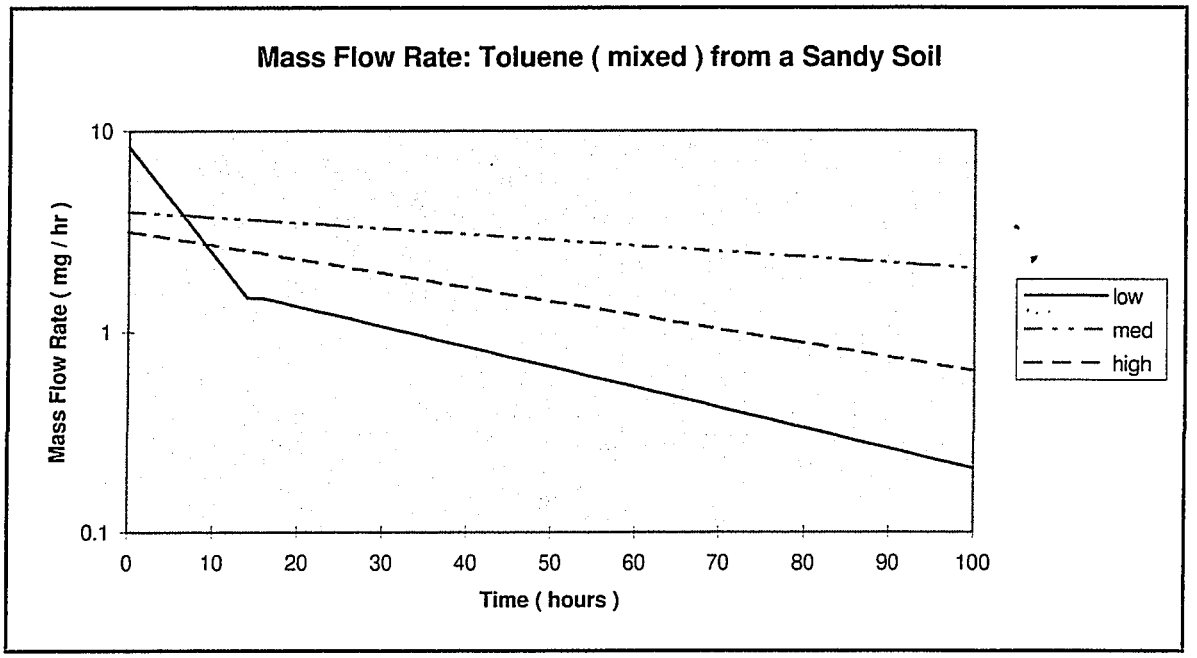


Figure 65 - Mass Flow Rate of Toluene from a mixture of BTEX in Sandy Soil

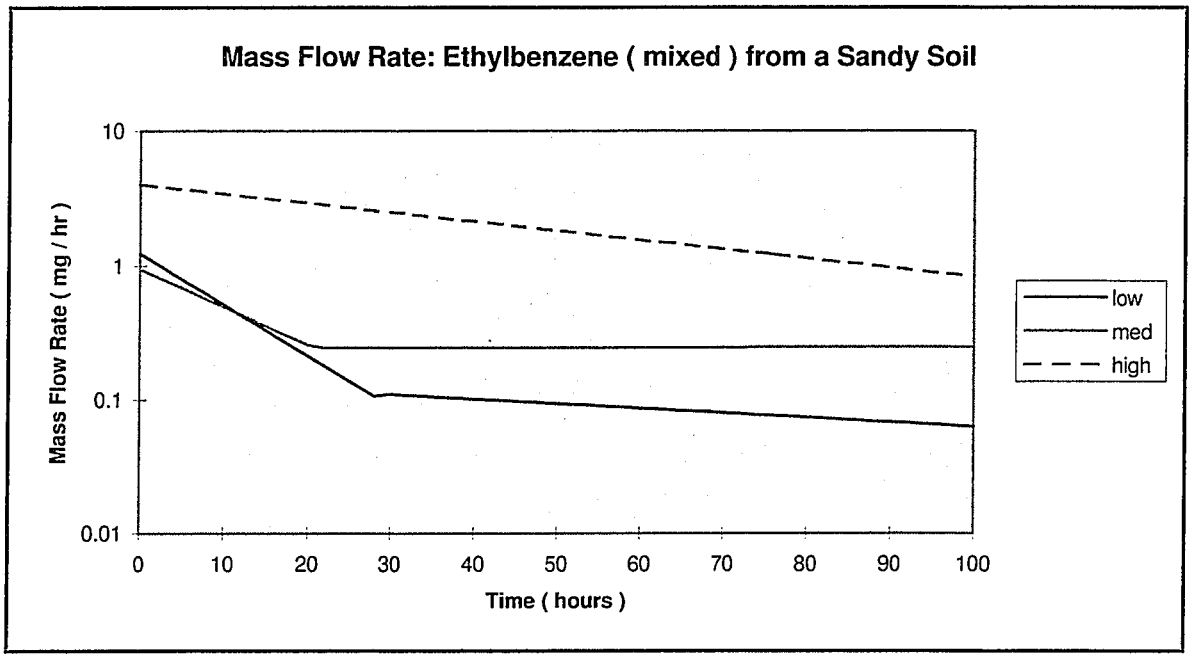


Figure 66 - Mass Flow Rate of Ethylbenzene from a mixture of BTEX in Sandy Soil

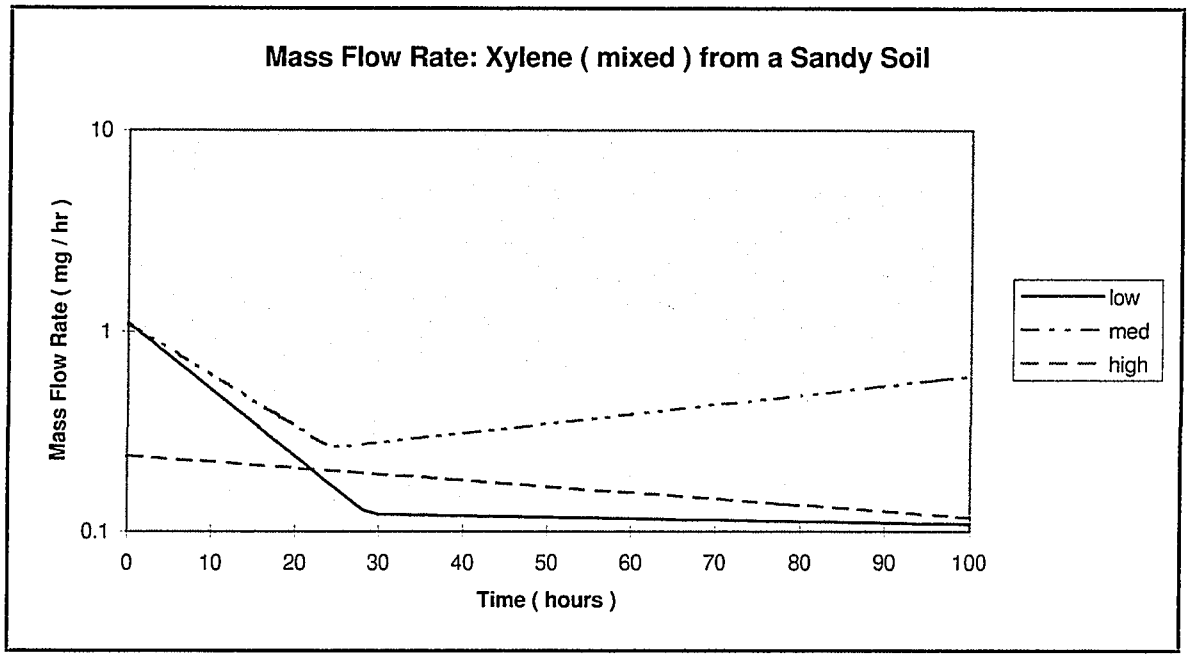


Figure 67 - Mass Flow Rate of Xylene from a mixture of BTEX in Sandy Soil

Stripping a mixture of benzene, toluene, xylene and ethylbenzene from sandy soil, showed little correlation between mass flow rate and air flow rate. The rate at which benzene was stripped was about 70% of rate observed when benzene was used alone. Toluene stripping rates were comparable but that is probably more indicative of a problem with the experiment conducted using toluene as a single compound. For both xylene and ethylbenzene, the stripping rates were very low and the residual concentrations, in the soils, were quite high. This indicates that the air flow rates used in this study were not sufficiently high to remove these two compounds when they were adsorbed to organic matter.

5.2.3.3 Stripping With Saturated Air

Figures 68 to 70 show typical curves for concentration versus time while using saturated air. The corresponding mass flow rate versus time at different air flow rates are shown in Figure 71.

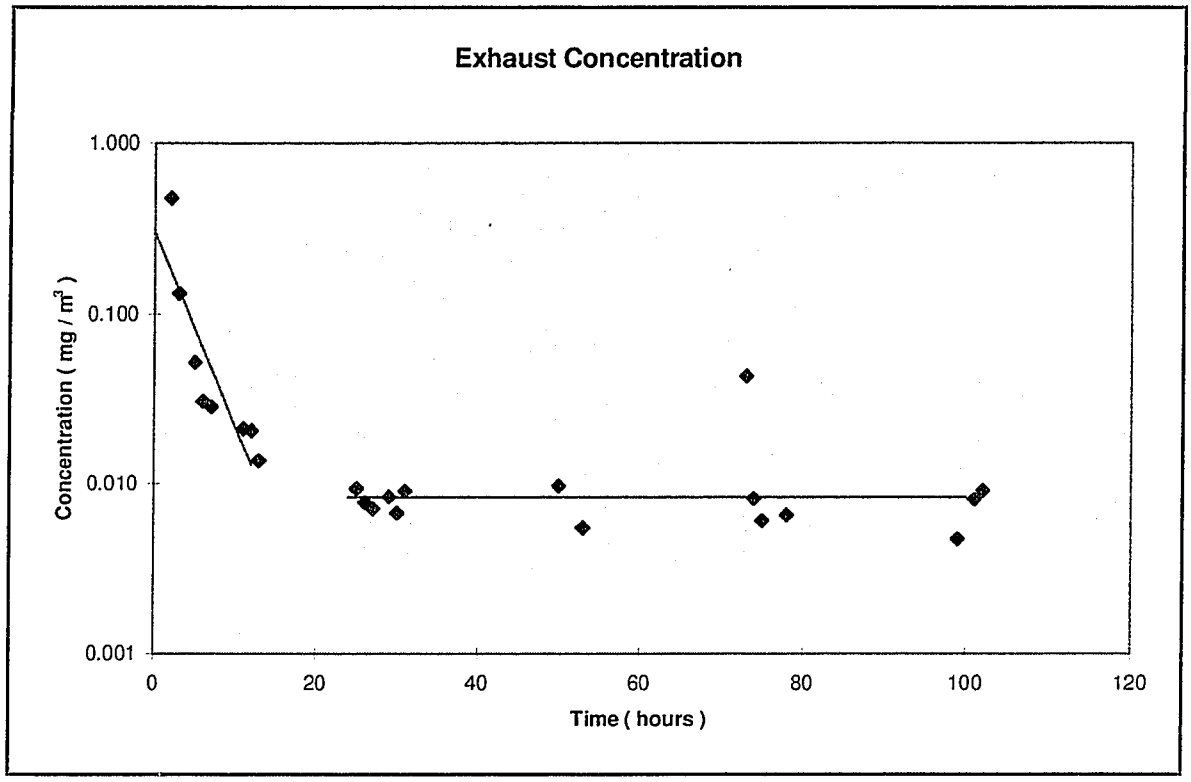


Figure 68 - Concentration of Toluene (Sat. Air) in a Sandy Soil (Q_{air} = 1.46 L/h)

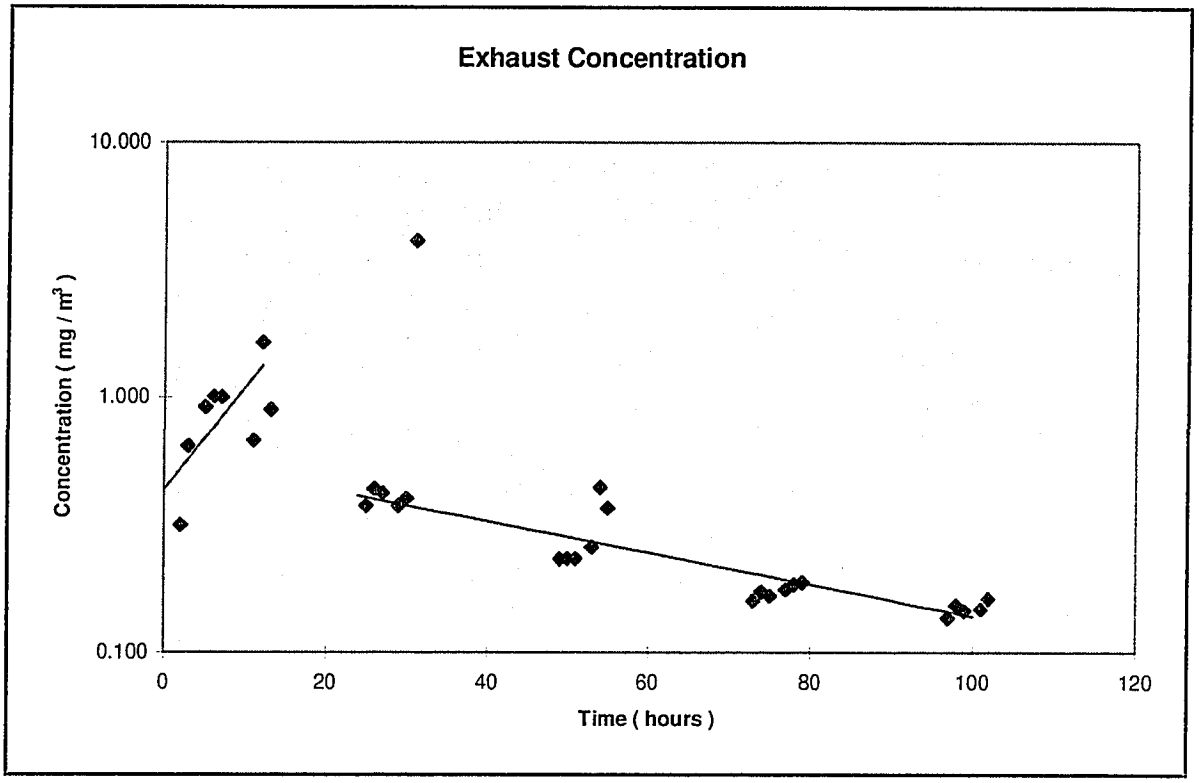


Figure 69 - Concentration of Toluene (Sat. Air) in a Sandy Soil (Q_{air} = 2.58 L/h)

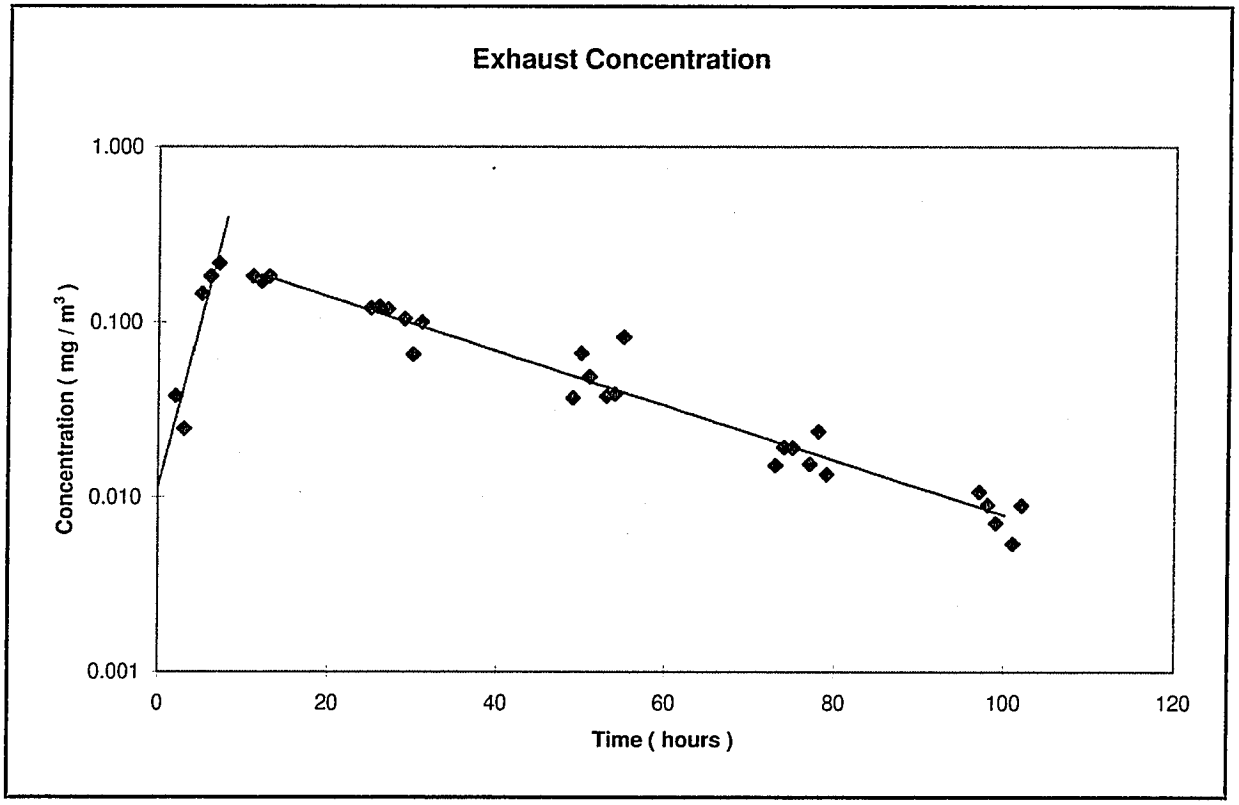


Figure 70 - Concentration of Toluene (Sat. Air) in a Sandy Soil (Q_{air} = 7.03 L/h)

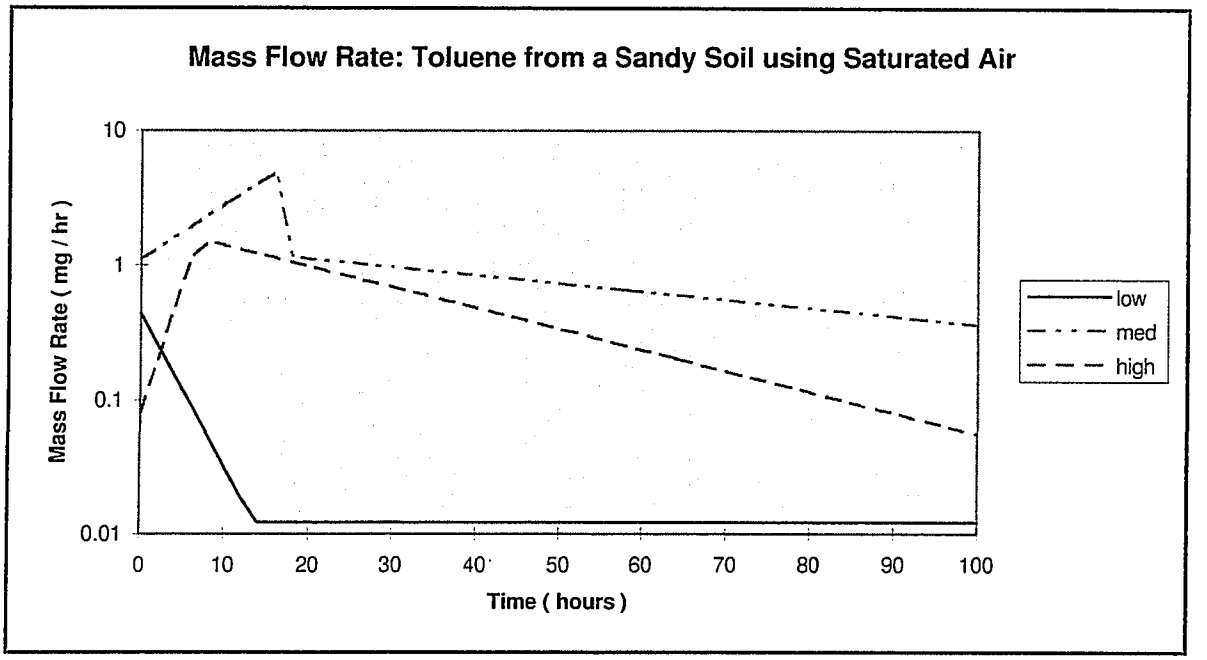


Figure 71 - Mass Flow Rate of Toluene from Sandy Soil stripped with Saturated Air

The three sandy soil columns that were stripped using saturated air, showed removal rates lower than that stripped with dry air. This was expected because as dry air flows through a soil column water is evaporated along with the volatile chemicals. This reduces the total pore water volume leading to higher relative concentrations of contaminates in the pore water. In turn, higher pore water concentrations result in higher air concentrations as partitioning occurs according to Henry's law.

5.2.3.4 Effect of Chemical Volatility

The effect of chemical volatility, on the mass flow rate, is shown in Figures 72 and 73. These figures clearly show that higher mass flow rates were obtained for chemicals with higher pure chemical vapour pressures, at the same air flow rates. The curve for toluene shows a steeper decline than the curves for xylene and ethylbenzene. This

indicates that mass of toluene in the column was quickly depleted, possibly indicating that a leak occurred during that particular experiment. Had and equal concentration of chemicals been available in all three columns, the one containing toluene would have exhibited a higher mass flow rate than xylene or ethylbenzene.

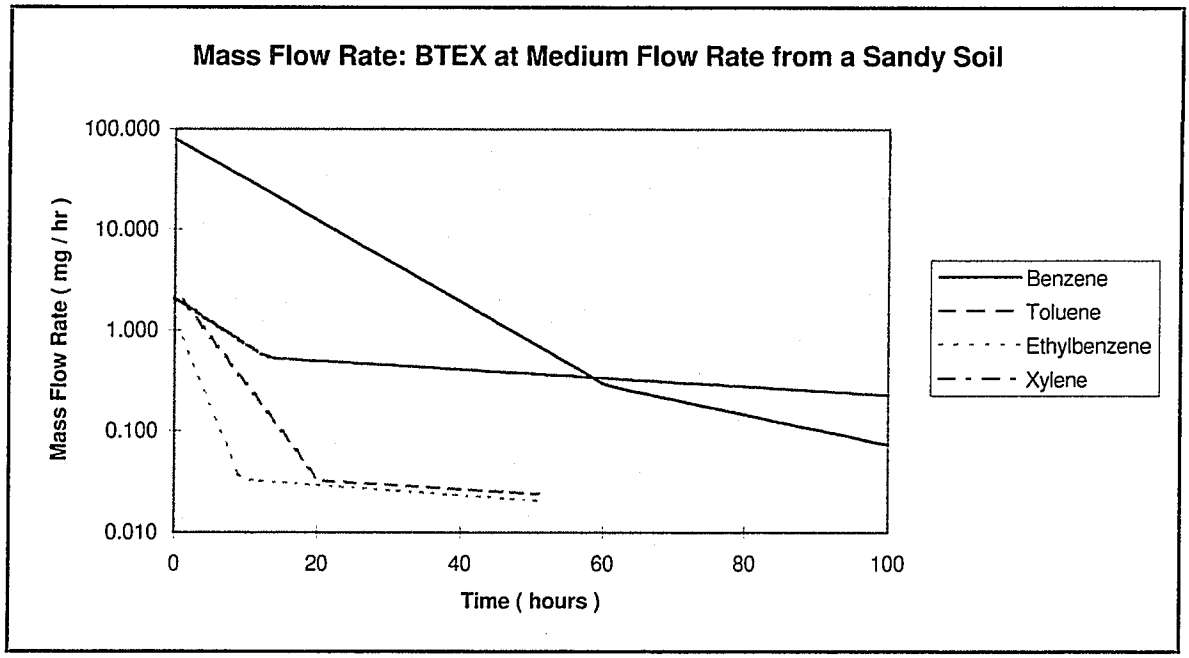


Figure 72 - Mass Flow Rate of BTEX from Sandy Soil at Medium Flow Rates

5.2.3.5 Effect of Moisture Content

The effect of moisture content can be seen when comparing the organic soil with the sandy soil. In the organic soil, which has a higher moisture content, when both toluene and xylene were stripped the exhaust concentrations were higher than the concentrations seen from the experiments using the sandy soil. Using benzene, exhaust concentrations seen in the sandy soil were higher indicating that high vapour pressures can overcome limitations existing in soils with high moisture contents.

5.2.3.6 Stripping Under Different Environmental Conditions

The only chemical that was used under all four different conditions of experiments was toluene. Consequently, this was chosen as a reference. A comparison of the stripping of toluene, in each of the four experiments conducted with a medium flow rate, is shown in Figure 73.

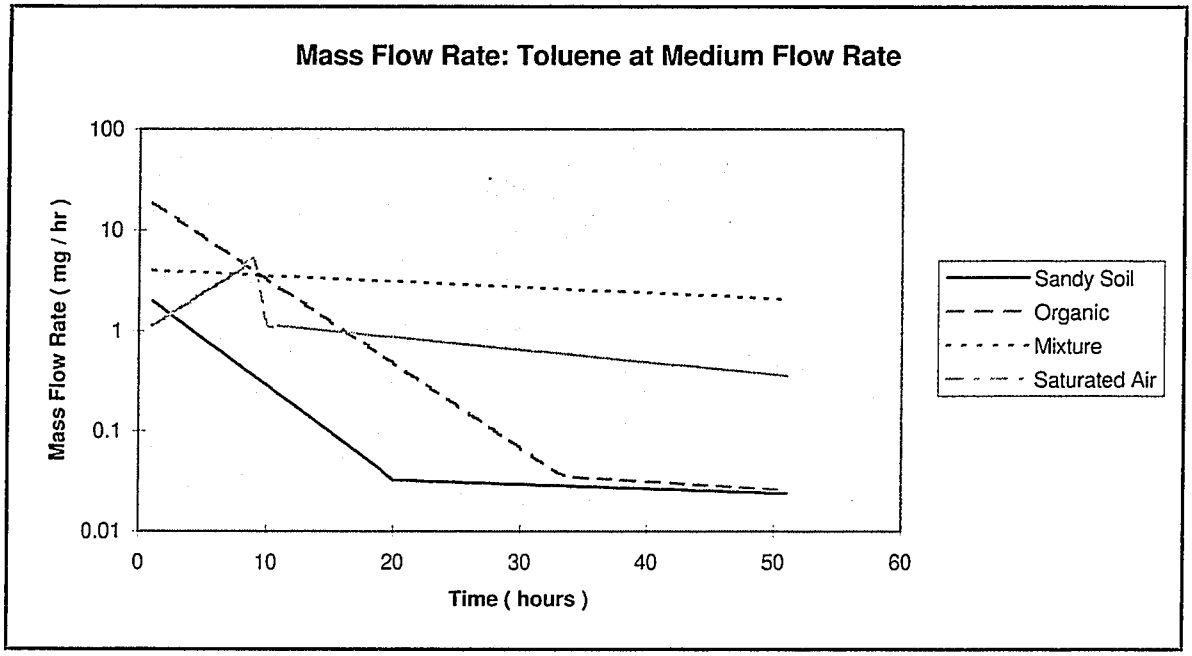


Figure 73 - Mass Flow Rate of Toluene at Medium Air Flow Rates

The mass flow rate of toluene from the organic soil was the highest. Toluene, added to the column as a mixture, exhibited a similar slope but about double the starting concentration obtained when stripped with saturated air. The low exhaust concentrations obtained with the sandy soil are again indicative of an unaccounted loss of toluene some time during the experiment. The curves from the sandy soil and the curve from the organic soil are similar in shape.

5.3 Mass Recovery Time

Another way of looking at the effectiveness of stripping during each experiment, is to compare the amount of mass recovered to the mass added. It was assumed that the solution added to each column was of uniform concentration and that the mass added to each column was equal to the product of solution concentration and volume of liquid added. It was also assumed that each of the three columns received equal amounts of the contaminants and moisture. These assumptions were not valid. In several cases, large positive or negative discrepancies occurred. The negative results were caused when the calculated mass removed was greater that the mass added.

Hayden *et al.* (1994) reported the same problem during similar experiments. They decided to use the area under the removal curves as an estimate of the initial mass added. During the experiments conducted in this study, the residual contaminant concentrations in the soil ,as well as the mass removed in the exhaust air, were calculated. A reasonable estimate of the initial mass in the columns was obtained by adding the mass removed in the exhaust air and the residual mass in the soil column.

The recovery and volume of air divided by volume of soil required for 90% and 95% removal of contaminants, under different conditions, are presented in Tables 23 and 24. Table 25 shows the time needed to reach the Ontario guidelines for surface soil clean-up in areas classified for residential or parkland use. Table 25 lists the time to reach the clean-up criteria for industrial properties.

Table 24 - Time Required to Achieve 90% Removal

		AIR FLOW RATE L/hr		
COMPOUND	MEDIA	LOW (Apr. 1.5)	MEDIUM (Apr. 3.0)	HIGH (Apr. 6.0)
Benzene	Sand	> 100	40	25.5
Toluene	Sand	> 100	> 100	> 100
Ethylbenzene	Sand	> 100	> 100	> 100
Xylene	Sand	> 100	> 100	> 100
Benzene	Organic	24	21	17
Toluene	Organic	75	25	> 100
Xylene	Organic	> 100	25	23
Mixture of all BTEX Compounds				
Benzene	Sand	98	98	24
Toluene	Sand	> 100	> 100	> 100
Ethylbenzene	Sand	> 100	> 100	> 100
Xylene	Sand	> 100	> 100	> 100
Saturated Air Used for Stripping				
Toluene	Sand	> 100	> 100	> 100

Table 25 - Time Required to Achieve 95% Removal

		AIR FLOW RATE L/hr		
COMPOUND	MEDIA	LOW (Apr. 1.5)	MEDIUM (Apr. 3.0)	HIGH (Apr. 6.0)
Benzene	Sand	> 100	> 100	30
Toluene	Sand	> 100	> 100	> 100
Ethylbenzene	Sand	> 100	> 100	> 100
Xylene	Sand	> 100	> 100	> 100
Benzene	Organic	31	24	21
Toluene	Organic	> 100	> 100	> 100
Xylene	Organic	> 100	> 100	48
Mixture of all BTEX Compounds				
Benzene	Sand	> 100	> 100	29
Toluene	Sand	> 100	> 100	> 100
Ethylbenzene	Sand	> 100	> 100	> 100
Xylene	Sand	> 100	> 100	> 100
Saturated Air Used for Stripping				
Toluene	Sand	> 100	> 100	> 100

Table 26 - Time Required to Meet Residential/Parkland Guidelines

		AIR FLOW RATE L/hr		
COMPOUND	MEDIA	LOW (Apr. 1.5)	MEDIUM (Apr. 3.0)	HIGH (Apr. 6.0)
Benzene	Sand	> 100	> 100	> 100
Toluene	Sand	> 100	> 100	> 100
Ethylbenzene	Sand	> 100	> 100	> 100
Xylene	Sand	> 100	> 100	> 100
Benzene	Organic	> 100	> 100	> 100
Toluene	Organic	> 100	> 100	> 100
Xylene	Organic	> 100	> 100	> 100
Mixture of all BTEX Compounds				
Benzene	Sand	> 100	> 100	> 100
Toluene	Sand	> 100	> 100	> 100
Ethylbenzene	Sand	26	> 100	> 100
Xylene	Sand	> 100	> 100	> 100
Saturated Air Used for Stripping				
Toluene	Sand	> 100	> 100	> 100

Table 27 - Time Required to Meet Industrial Property Guidelines

		AIR FLOW RATE L/hr		
COMPOUND	MEDIA	LOW (Apr. 1.5)	MEDIUM (Apr. 3.0)	HIGH (Apr. 6.0)
Benzene	Sand	> 100	> 100	> 100
Toluene	Sand	0	0	0
Ethylbenzene	Sand	0	0	0
Xylene	Sand	0	0	0
Benzene	Organic	24	21	21
Toluene	Organic	0	0	0
Xylene	Organic	0	0	0
Mixture of all BTEX Compounds				
Benzene	Sand	> 100	> 100	100
Toluene	Sand	0	0	0
Ethylbenzene	Sand	0	0	0
Xylene	Sand	0	0	0
Saturated Air Used for Stripping				
Toluene	Sand	0	0	0

5.3.1 Cumulative Mass Fraction Removed

When presenting removal rates as mass fractions, the impact of variations in the concentrations initially added to different columns is reduced. In addition, the fraction of contaminants that still remained in the soil columns at the end of each experiment is clearly presented. When the slope of the removal curves level off, indicating very low exhaust

concentrations, it can be assumed that the remaining mass will not be feasibly removed using the soil vapour extraction method.

5.3.1.1 Stripping of Individual Contaminants

The contaminant mass fraction removed, for individual contaminants, in each set of experiments is presented in Figures 74 to 86. The mass fraction removed, for each data set, was determined by dividing cumulative mass removed by the estimated total mass added to each column.

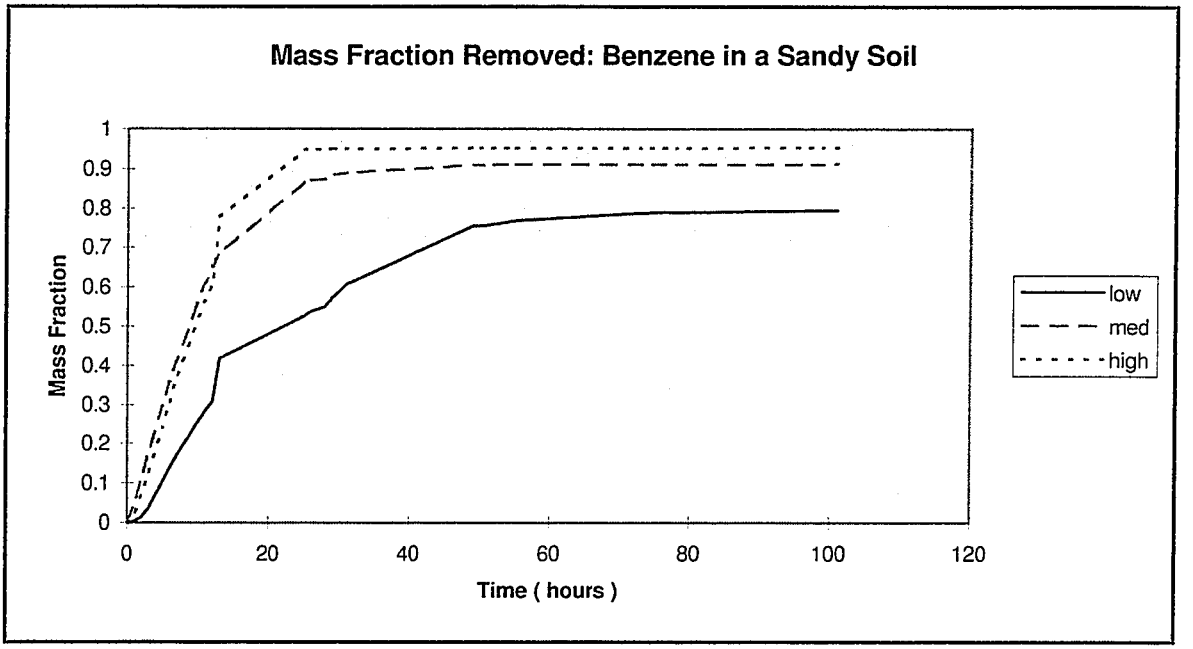


Figure 74 - Mass Fraction of Benzene Removed from Sandy Soil

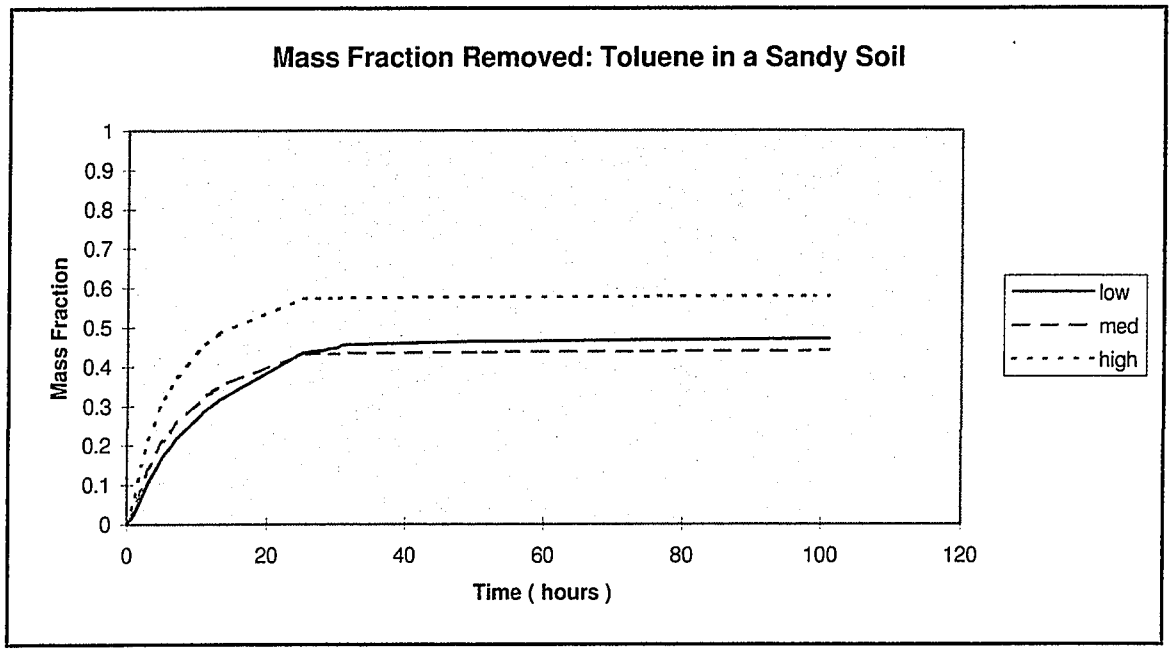


Figure 75 - Mass Fraction of Toluene Removed from Sandy Soil

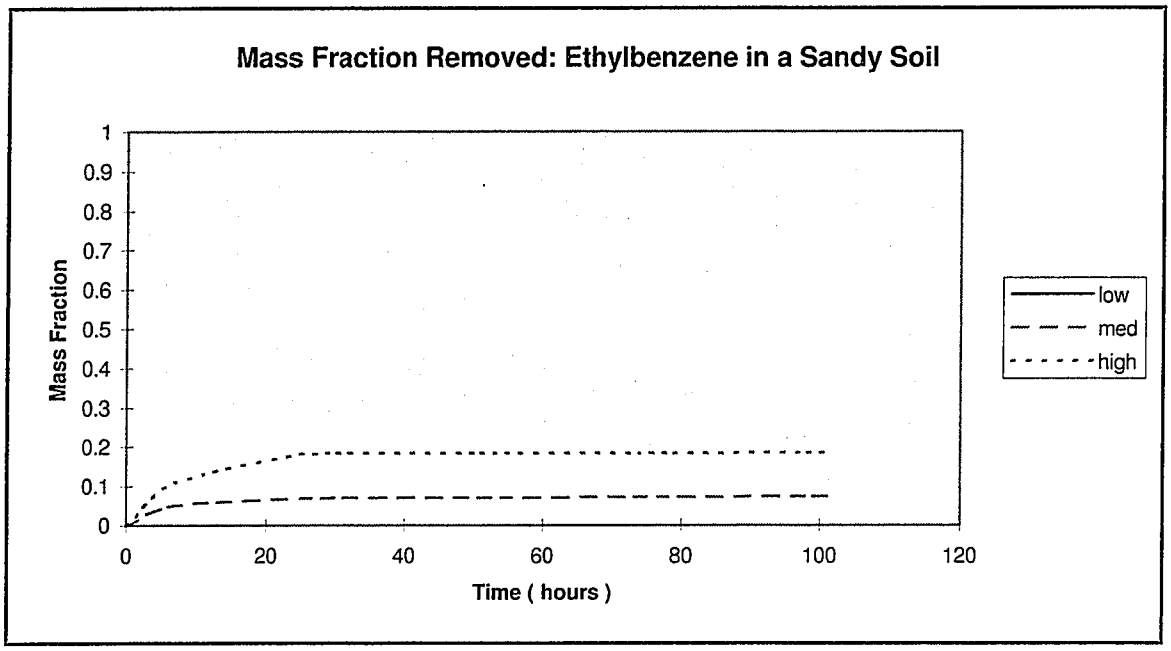


Figure 76 - Mass Fraction of Ethylbenzene Removed from Sandy Soil

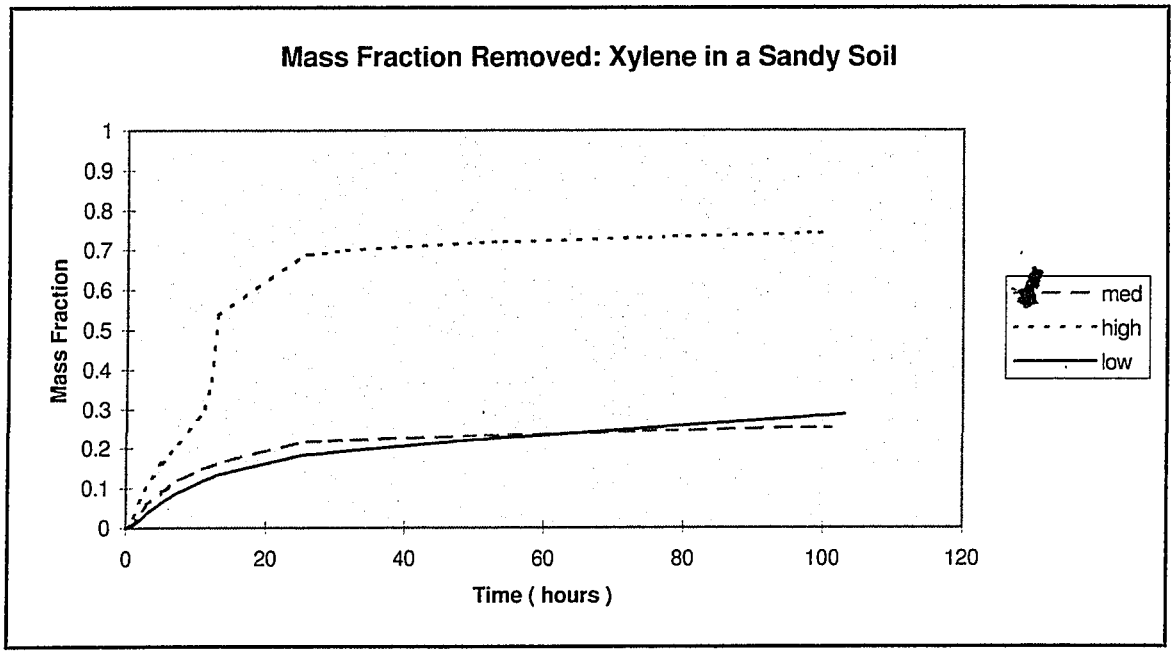


Figure 77 - Mass Fraction of Xylene Removed From Sandy Soil

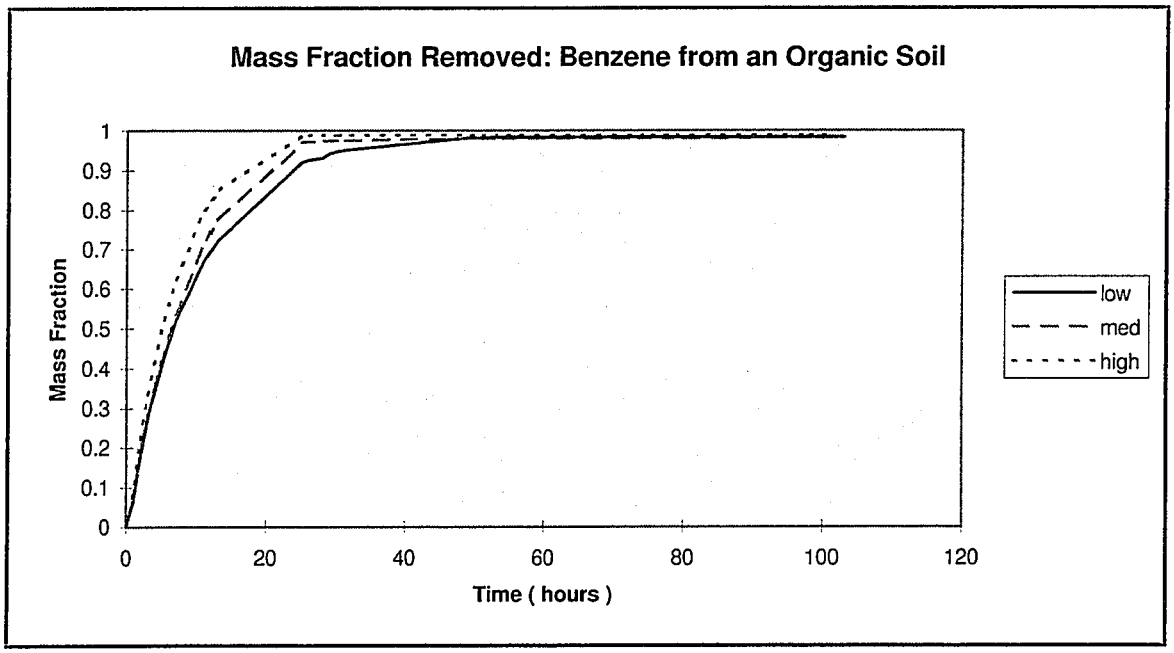


Figure 78 - Mass Fraction of Benzene Removed from Organic Soil

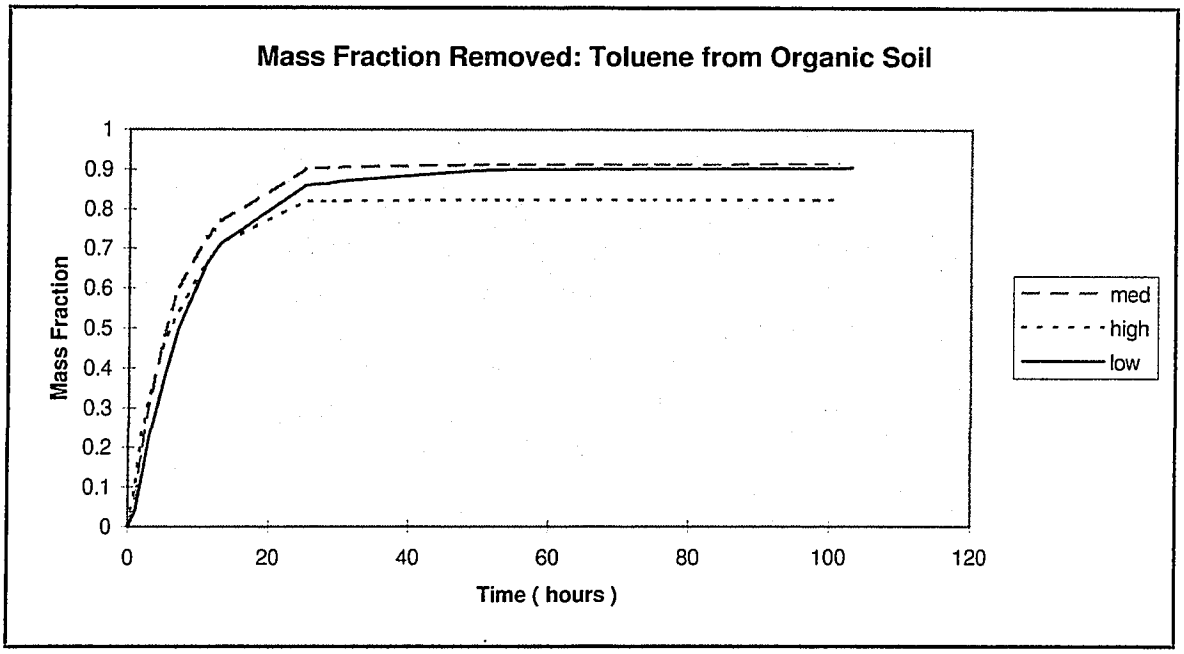


Figure 79 - Mass Fraction of Toluene Removed from Organic Soil

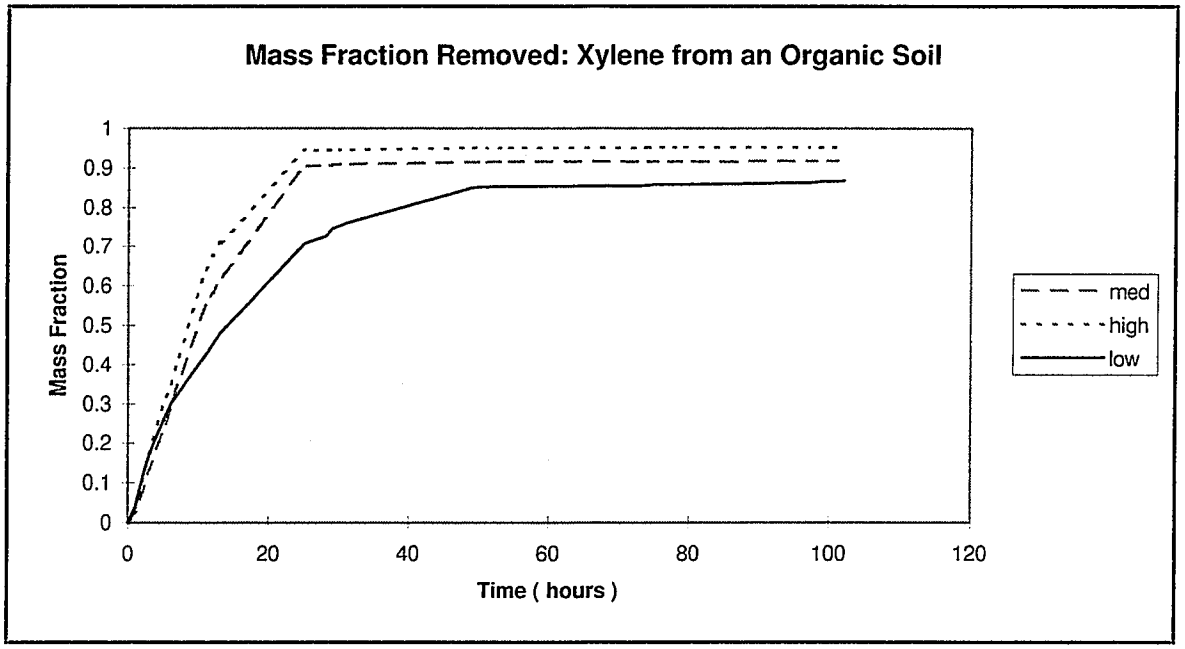


Figure 80 - Mass Fraction of Xylene Removed from Organic Soil

When single contaminants were applied to the sandy soil, it was observed that, at higher air flow rates, contaminants were removed at faster rates and resulted in lower residual concentrations. In the sandy soil containing benzene, toluene, xylene and ethylbenzene more than 95% of the easily removable fraction of the contaminant mass was removed within 24 hours. However, the fraction of the contaminant mass retained by the sandy soil varied considerably, with the highest value for ethylbenzene and the lowest for benzene.

The columns containing organic soils exhibited higher removable fraction as compared to the sandy soil. In each of the experiments, with benzene, toluene and xylene, air flow rate appeared to have no appreciable effect on the mass fraction recovered. The mass fraction recovered from the columns containing benzene was more than 0.98, where as for toluene and xylene recovery rates were nearly 0.90, for all three air flow rates. The recovery curves for Xylene show faster removal at higher air flow rates. For all columns containing the organic soil, more than 95% of the easily removable fraction of the contaminant mass was removed within 20 hours.

5.3.1.2 Stripping of Contaminant Mixture

Figures 81 to 84 show the effect of stripping BTEX as a mixture from sandy soil, at three different flow rates. No clear correlation between flow rate and mass fraction removed was observed. This is an indication that the stripping of contaminants from a mixture is rate limited.

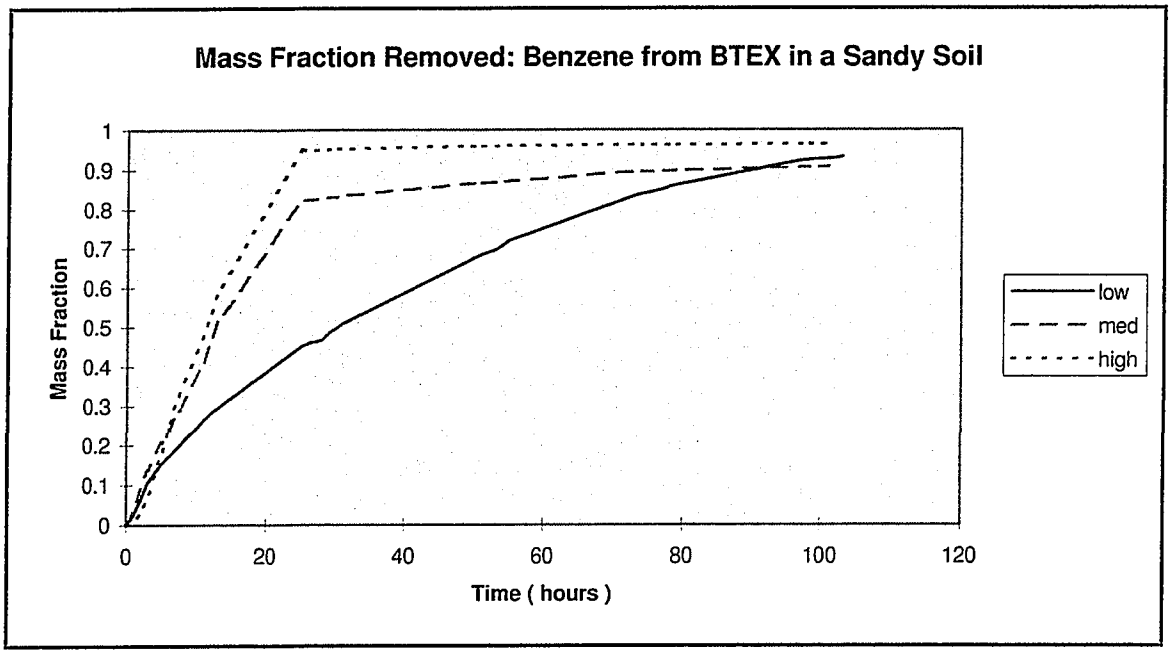


Figure 81 - Mass Fraction of Benzene Removed from a mixture of BTEX in Sandy Soil

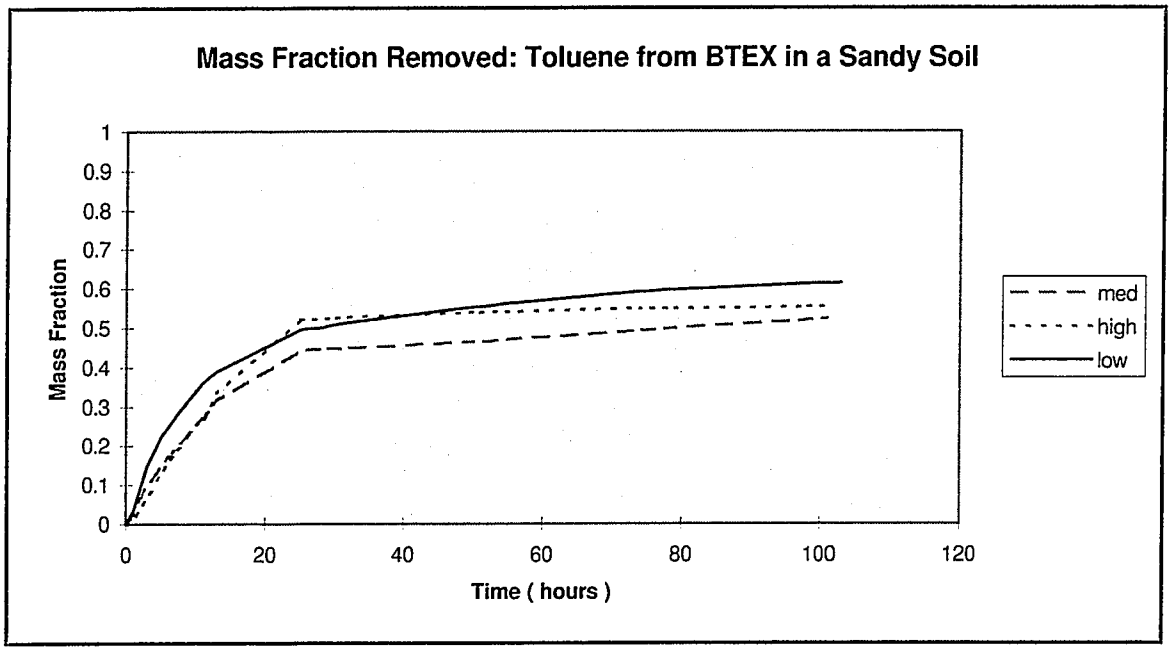


Figure 82 - Mass Fraction of Toluene Removed from a mixture of BTEX in Sandy Soil

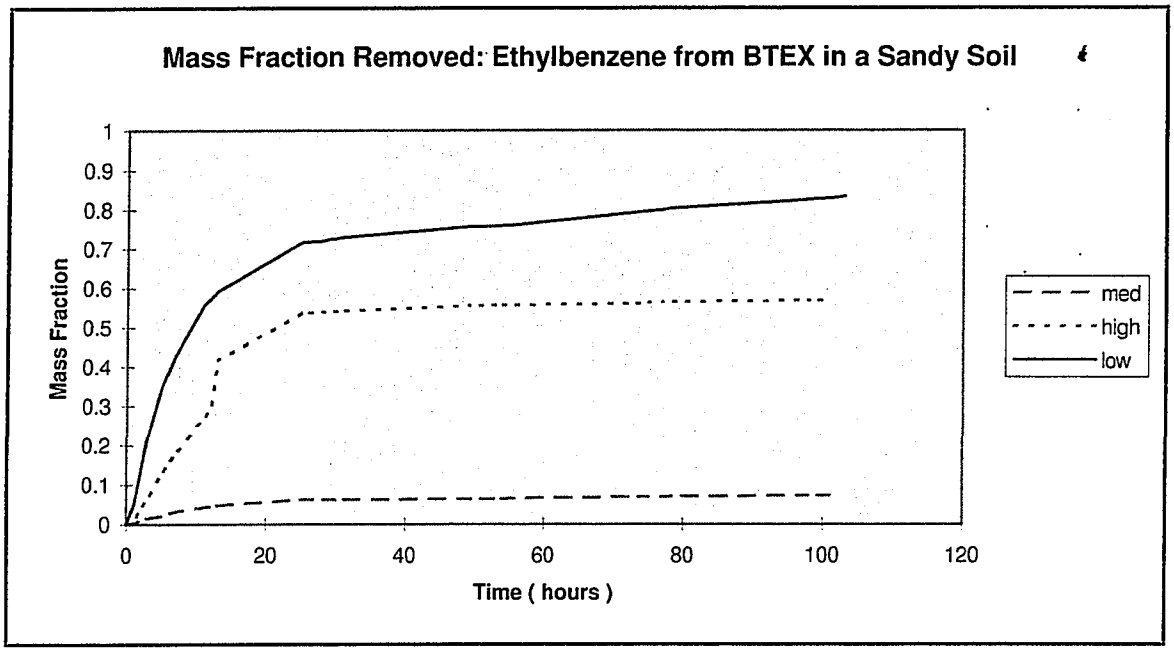


Figure 83 - Mass Fraction of Ethylbenzene Removed from a mixture of BTEX in Sandy Soil

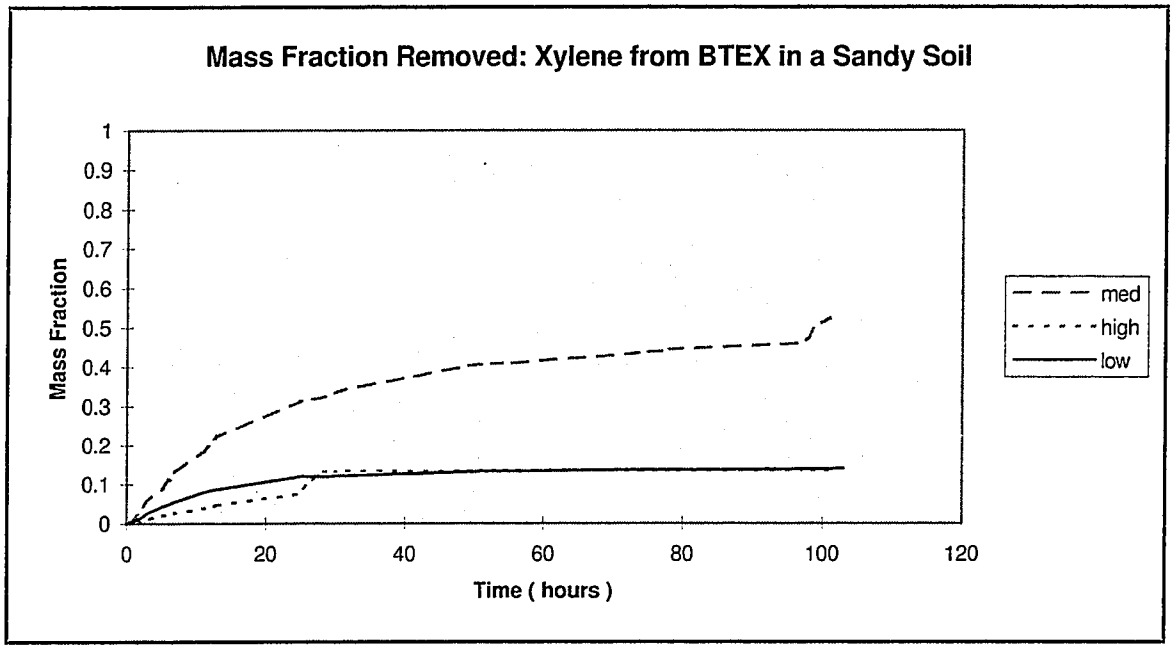


Figure 84 - Mass Fraction of Xylene Removed from a mixture of BTEX in Sandy Soil

5.3.1.3 Stripping with Saturated Air

Figure 85 shows the mass fraction of toluene removed from sandy soil using moisture-saturated air.

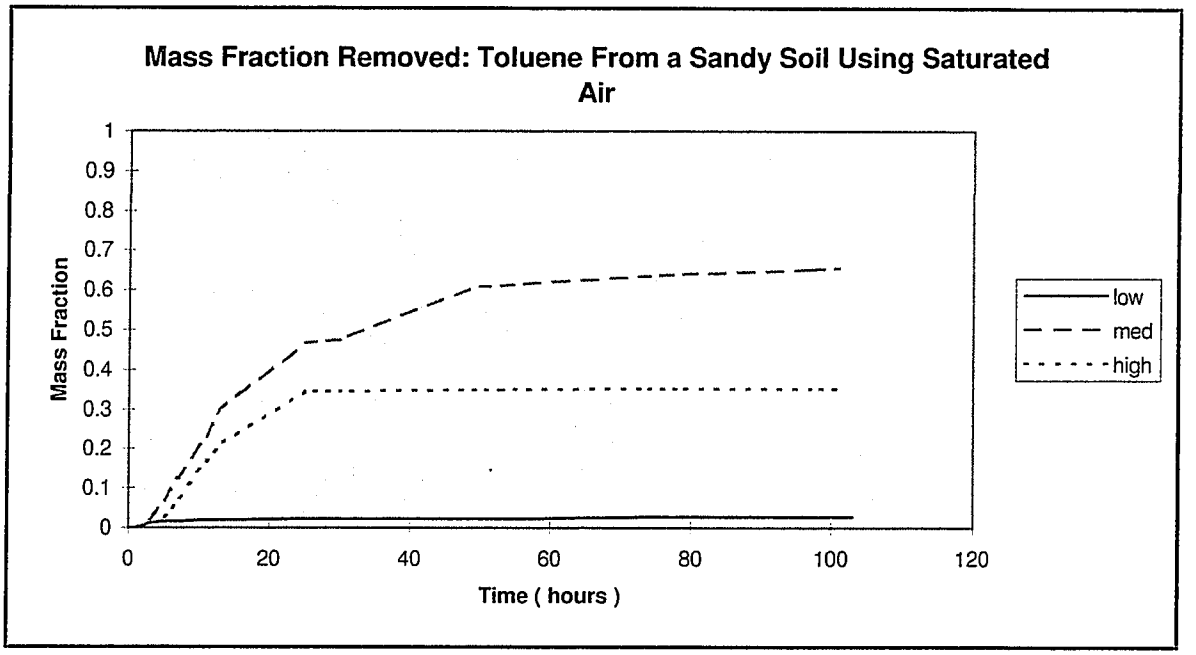


Figure 85 - Mass Fraction of Toluene Removed from Sandy Soil using Saturated Air

The three experiments conducted with sandy soil at a medium flow rate, using toluene as an individual contaminant with dry air and saturated air as well as BTEX mixture in dry air, resulted in nearly equal mass fractions removed in 24 hours. After this time, the removal from the sandy soil, stripped with dry air, increased very slowly. However, both the column stripped with saturated air and the column containing BTEX continued to show further removal at a slow rate until 100 hours, when the experiments were ended.

The column stripped using saturated air was expected to show a slower rate of removal because the relative concentration in the pore water was less than would be

encountered if soil moisture was reduced during the course of the experiments. The residual concentration the saturated-air stripped column is expected to be lower because the soil will not dry out and therefore adsorption to mineral surfaces is negligible. The time to reach a final residual concentration will be much longer

5.3.1.4 Effect of Chemical Volatility

Figure 86 shows the comparison of the mass removal rates of the four BTEX components, stripped individually from the sandy soil. The more volatile compounds are removed faster and ultimately leave relatively smaller residual concentrations in the soil. The results may show lower recovery rates of ethylbenzene and xylene because both compounds are less soluble in water and are more susceptible to losses during experimentation.

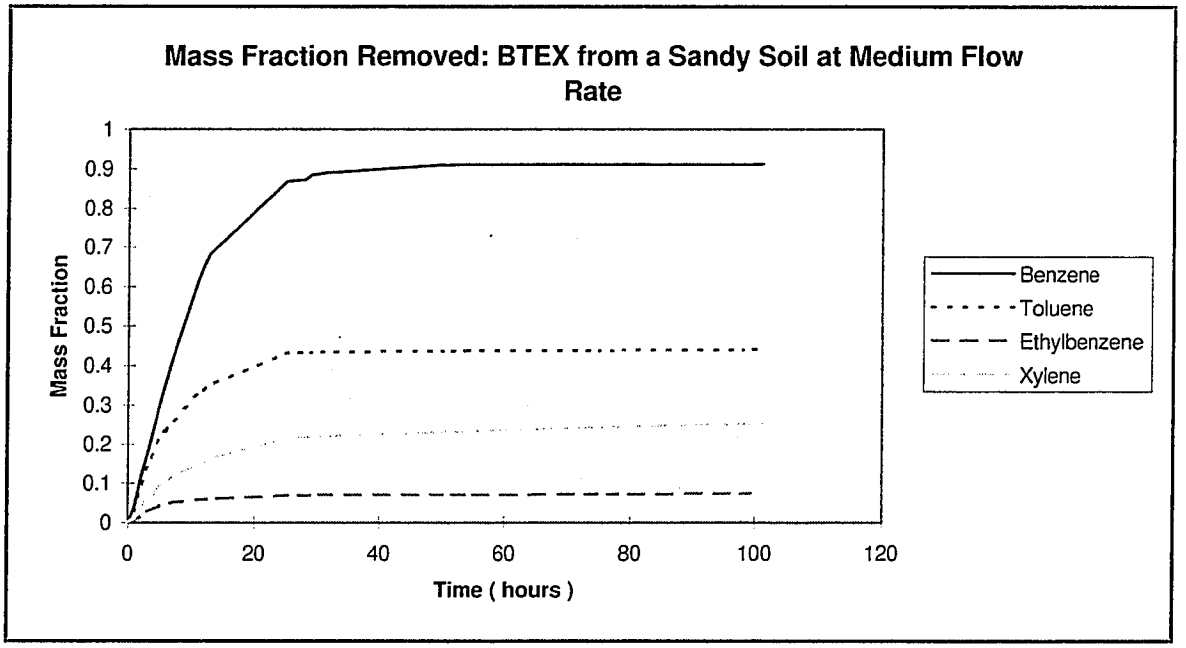


Figure 86 - Mass Fraction of BTEX Removed From Sandy Soil at a Medium Flow Rate

5.3.1.5 Effect of Moisture Content

It is likely that the higher recovery rates observed with organic soils were due to the higher porosity and moisture content in that soil. Both factors can result in increased dispersion through the column.

5.3.1.6 Stripping Under Different Environmental Conditions

Toluene, when stripped under various conditions, showed significant behavioural differences, as can be seen in Figure 87. When stripped from both sandy soil and an organic soil the mass fraction removal curve almost levelled off after 24 hours. However, the fraction removed from the organic soil was approximately 0.9, while the fraction removed from the sandy soil was only 0.4. This can be attributed to the porosity and moisture content differences between the two soils.

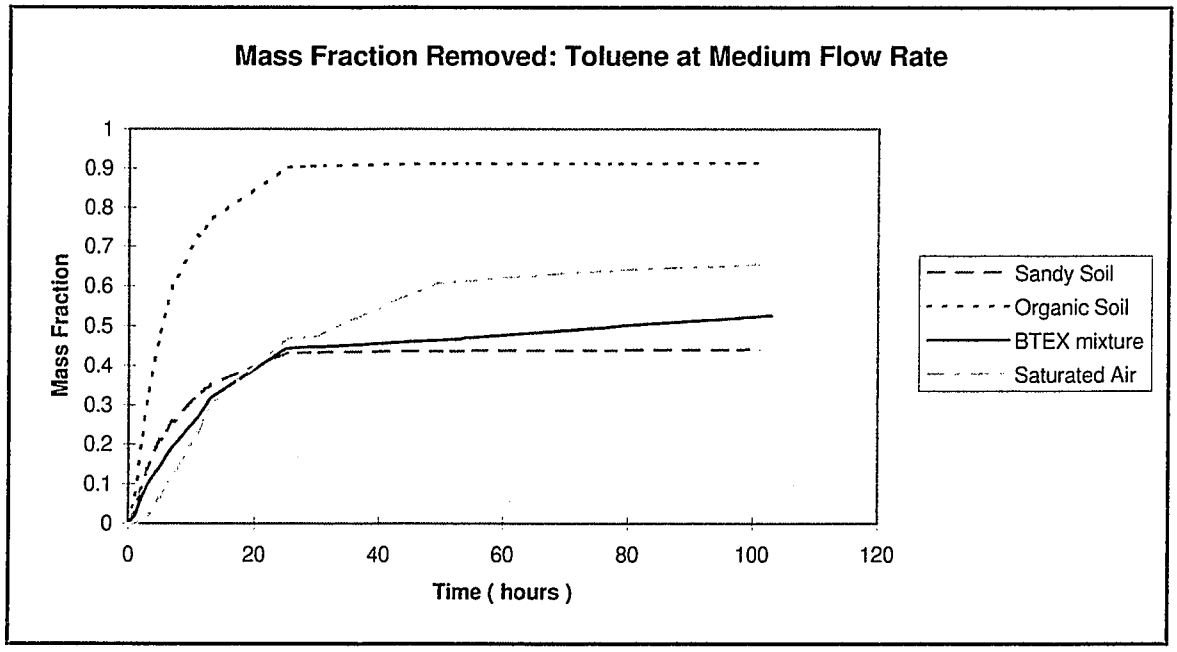


Figure 87 - Mass Fraction of Toluene Removed Under Various Environmental Conditions

5.4 Residual Concentrations in Soils

The analysis for the distribution of residual contaminants in the experimental soil columns was essential in determining the effectiveness of the stripping process. The residual concentrations were compared to the legislated levels in Ontario to gauge the ultimate effectiveness of stripping. Final moisture distribution was also determined and documented for two reasons. First, all of the soil concentrations reported in this document are on a dry basis, so moisture levels are needed for concentration calculations. Secondly, the literature shows that the moisture content can effect the sorption behaviour of chemicals in the subsurface environment and is therefore needed in order to interpret the experimental results (Farmer *et al.*, 1980).

5.4.1 Initial Concentrations

Initially, when compounds were added to the soils, it was assumed that both the moisture and the contaminants were evenly distributed throughout the columns. Table 27 shows the initial contaminant concentrations and moisture levels based on the assumptions that the final moisture content was the sum of the moisture content as received and the volume of contaminant solution added to the columns and the concentrations of the contaminant solutions were exactly 150 mg/L.

5.4.2 Residual Water Distribution

The residual water distributions in the sand columns in all experiments were similar in shape, with higher concentrations at the bottom of the columns and gradually decreasing upwards. Figure 88, shows the final moisture distribution in the sandy soil that

contained toluene and was run at a medium air flow rate. It is typical of most of the experiments with sandy soil. The moisture content was higher at the bottom of the column because once flow had been initiated, at the beginning of an experiment, some moisture was forced out of pore spaces and subsequently drained under the force of gravity, to the bottom of the columns.

Table 28 - Calculated Initial Uniform Moisture and Contaminate Concentrations

INITIAL CONCENTRATIONS		Volume of Water Added (L)	Calculated Moisture Content (%)	Calculated Contaminant Concentration (µg / g)
COMPOUND	MEDIA			
Benzene	Sand	1.83	17.8	26.8
Toluene	Sand	1.51	14.9	22.3
Ethylbenzene	Sand	1.48	14.6	21.8
Xylene	Sand	1.62	16.0	24.0
Benzene	Organic	0.72	48.3	26.8
Toluene	Organic	1.03	55.9	38.2
Xylene	Organic	1.49	67.3	55.3
Mixture of all BTEX Compounds				
Benzene	Sand	0.953	9.4	14.0
Toluene	Sand	0.953	9.4	14.0
Ethylbenzene	Sand	0.953	9.4	14.0
Xylene	Sand	0.953	9.4	14.0
Saturated Air Used for Stripping				
Toluene	Sand	2.16	21.3	31.9

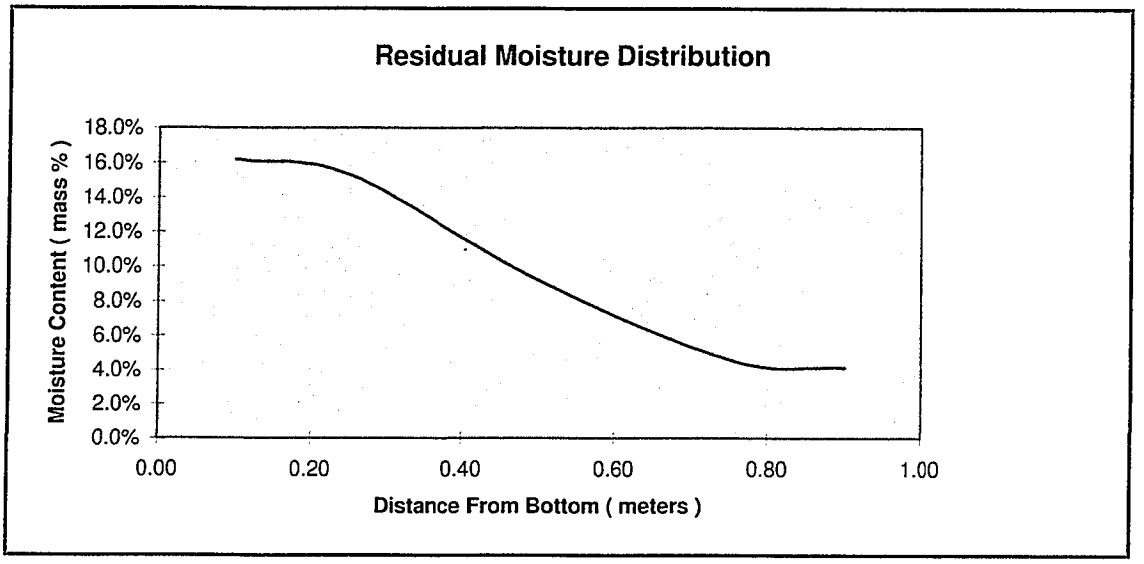


Figure 88 - Typical Residual Moisture Distribution in Sandy Soil

The moisture distribution in the organic soil exhibited a different shape. The moisture concentration was constant through most of the column and there was a slight decrease near the exit end. This was because of the fact that organic soil can hold moisture more tightly because of the higher porosity as compared to sandy soil. Figure 89 shows a typical moisture distribution in an organic soil and was obtained from the experiment conducted with toluene.

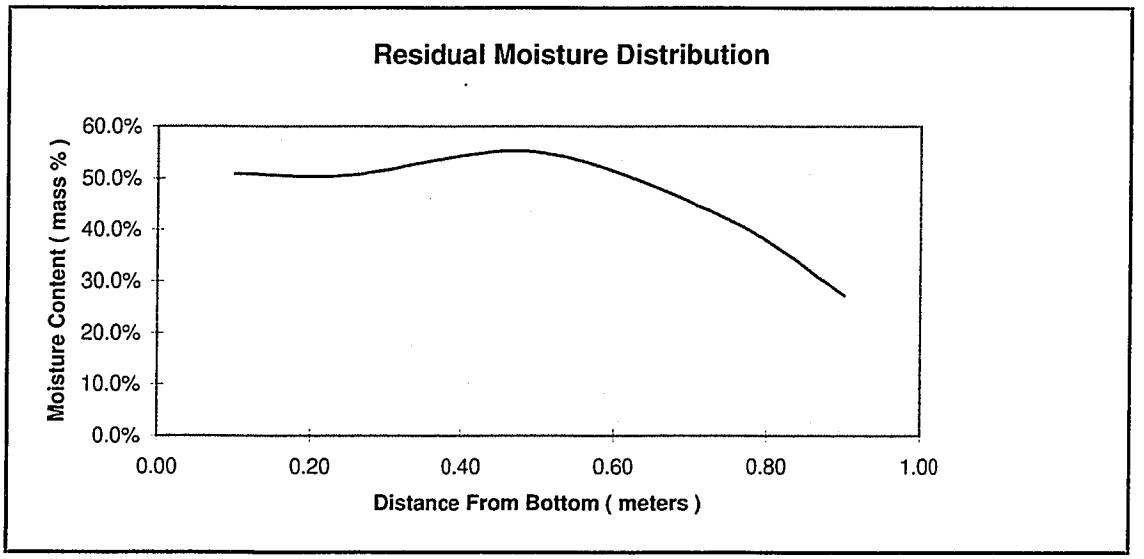


Figure 89 - Typical Residual Moisture Distribution in an Organic Soil

The highest and lowest residual moisture concentrations obtained in each experiments conducted are presented in Table 28. These values were selected without consideration of the location within the columns. Detailed information for each experiment can be found on the attached disk.

Table 29 - Range of Residual Water Content in Soil

RESIDUAL WATER CONTENT (%)		AIR FLOW RATE L/hr		
COMPOUND	MEDIA	LOW (≈ 1.5)	MEDIUM (≈ 3.0)	HIGH (≈ 6.0)
Benzene	Sand	16.6 - 15.7	16.7 - 4.6	14.7 - 4.5
Toluene	Sand	16.2 - 4.1	16.1 - 4.0	15.7 - 4.5
Ethylbenzene	Sand	19.4 - 9.2	12.6 - 4.4	18.6 - 4.9
Xylene	Sand	17.3 - 4.5	18.1 - 4.6	17.4 - 3.1
Benzene	Organic	58.3 - 48.1	56.9 - 38.8	57.0 - 49.8
Toluene	Organic	55.0 - 27.2	50.0 - 38.7	51.2 - 39.3
Xylene	Organic	46.5 - 44.1	48.7 - 44.2	47.3 - 41.7
Mixture of BTEX Compounds				
Benzene	Sand	6.5 - 5.0	14.0 - 4.1	15.1 - 5.1
Toluene	Sand	6.5 - 5.0	14.0 - 4.1	15.1 - 5.1
Ethylbenzene	Sand	6.5 - 5.0	14.0 - 4.1	15.1 - 5.1
Xylene	Sand	6.5 - 5.0	14.0 - 4.1	15.1 - 5.1
Saturated Air Used for Stripping				
Toluene	Sand	13.8 - 6.6	14.3 - 4.5	11.7 - 4.3

5.4.3 Residual Contaminant Distribution

Residual contaminant concentrations were higher near the inlet side of the columns in most of the experiments. A few concentration profiles contained dips and rises which indicated a drop and then increase in concentration towards the outlet. Variations such as

these can be expected in any soil analysis, and should not be considered to effect the trend. The typical residual concentration curve exhibited an almost constant, high concentration near the inlet and a much lower concentration near the outlet. Figure 90 shows a distribution in a nearly clean sandy soil to which toluene was applied and subsequently stripped at a low air flow rate, whereas Figure 91 was obtained for toluene in a mixture of BTEX stripped at a low air flow rate and in the middle stages of the stripping process.

The high and low residual contaminant concentrations for each experiment are shown in Table 30. This shows the best and worst case for each set of experimental conditions. When soil samples are collected in the field and analysed for guideline compliance when a single sample fails to meet the legislated levels any soil from the sampling point to a point where contaminant levels are acceptable is considered to not be in compliance. The concentrations of contaminants in all the columns where reduced below the guideline values with some samples taken from the majority of the columns, cleaned to the potable water/residential standards. The lowest concentrations found in most samples were 2 to 3 orders of magnitude higher than the Ontario background levels, leaving doubt that these levels could ever be met by using SVE only.

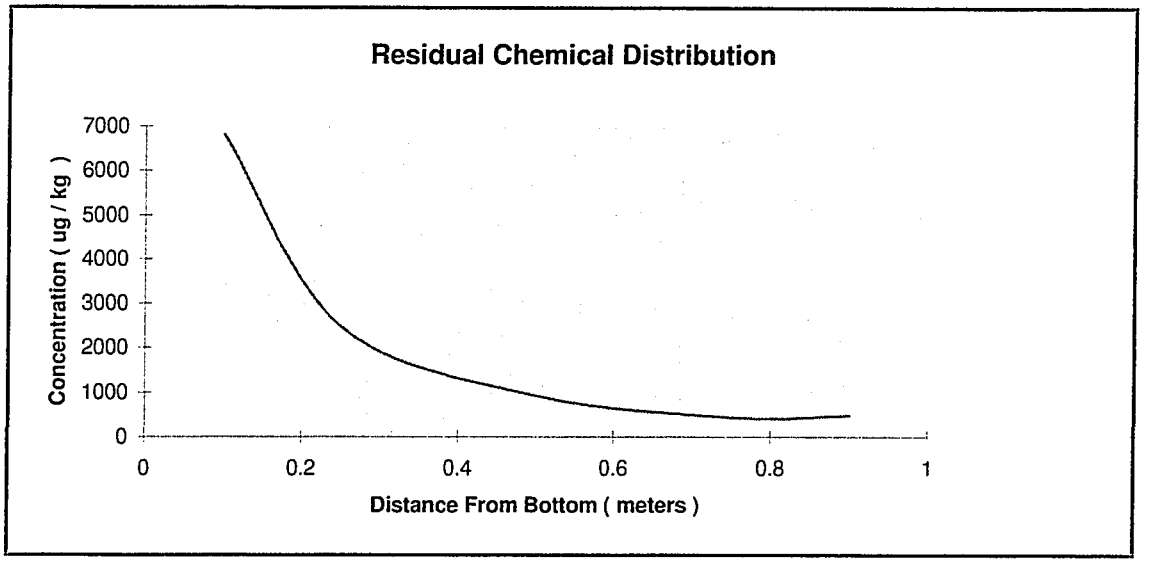


Figure 90 - Typical Residual Contaminant Profile Near the End of Stripping for Benzene in a Sandy Soil

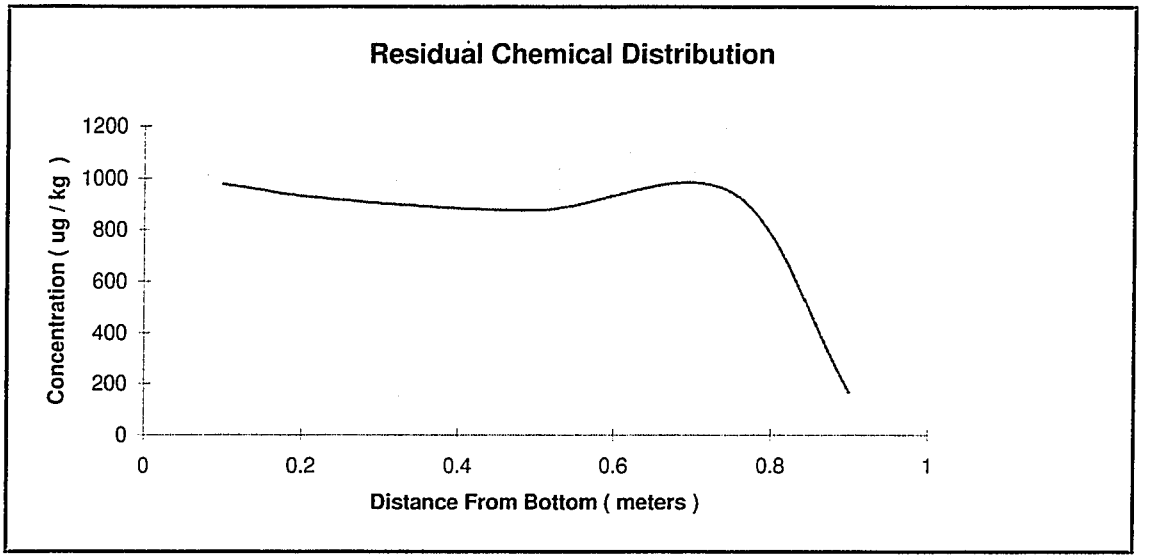


Figure 91 - Typical Residual Concentration Profile During Stripping Process with Toluene in BTEX in Sandy Soil

Table 30 - Range of Residual Contaminant Concentrations in Soil

RESIDUAL CONCENTRATIONS (µg / g)		AIR FLOW RATE L/hr		
COMPOUND	MEDIA	LOW (≈1.5)	MEDIUM (≈ 3.0)	HIGH (≈ 6.0)
Benzene	Sand	7.020 - 0.551	5.866 - 0.784	5.093 - 0.238
Toluene	Sand	5.770 - 0.376	5.890 - 0.224	5.994 - 0.188
Ethylbenzene	Sand	9.959 - 1.305	7.368 - 0.557	20.342 - 1.217
Xylene	Sand	6.502 - 1.630	15.290 - 1.403	1.568 - 1.386
Benzene	Organic	0.603 - 0.089	1.870 - 0.034	1.097 - 0.055
Toluene	Organic	11.456 - 0.081	13.355 - 0.326	35.377 - 0.307
Xylene	Organic	4.688 - 0.764	2.970 - 0.903	1.509 - 1.047
Mixture of BTEX Compounds				
Benzene	Sand	5.299 - 1.755	6.058 - 2.022	5.325 - 0.544
Toluene	Sand	6.113 - 1.042	7.605 - 6.396	7.291 - 0.937
Ethylbenzene	Sand	1.005 - 0.404	24.849 - 0.539	7.785 - 0.370
Xylene	Sand	19.713 - 0.815	1.689 - not det.	12.521 - 0.113
Saturated Air Used for Stripping				
Toluene	Sand	5.941 - 3.503	7.645 - 1.105	7.280 - 1.388

The standard for benzene concentrations in the soil on a property, which is being remediated to potable water standards, is the lowest non-background standard, of all the four compounds. The lowest concentrations obtained in the column containing the organic soil were slightly higher than the guideline values. With additional stripping time, the residual concentrations would have fallen below the guideline values. On the other hand, the columns containing sandy soil and benzene had low concentrations approximately 4 times the accepted value. Since the moisture content of the sand columns was relatively high at the conclusion of the experiments, there was no reason to assume

that mineral surface sorption was occurring. The explanation for the high residual concentrations is that sand had a lower porosity and therefore was less efficiently stripped. Further evidence of this is the fact that benzene was still detectable in the effluent from the sandy soil at the end of 5 days while in the organic soil no benzene was detected after that period. Since benzene concentrations were still detectable in the effluent from the sand column, it is expected that with an extended stripping time, the guidelines levels would be realised.

5.4.4 Comparison of Residual Contaminant Concentrations

The residual contaminant concentrations recorded for each experiment were compared to the concentrations in other experiments using paired-sample t-tests (Miller et. al., 1990). The t-test is used to determine if a significant difference exists between two sets of data. When the t value calculated using two sets of data is greater than a critical t value it can be concluded that the two sets of data are unique. The level of significance used in the t-tests presented below was 0.05.

5.4.4.1 Affect of Flow Rate on Residual Concentrations

Table 31 shows the t-test determined when comparing low to medium and medium to high air flow rates for each of the sets of experiments conducted. The value in brackets is t-critical and the tests that showed significant variations between the two data sets are highlighted. It can be seen that only the experiment using benzene and toluene in a mixture showed a significant decrease in the residual concentration when the air flow rate was increased from a medium rate to a high rate.

Table 31 - t-test Results for Comparison of Residual Concentrations at Different Flow Rates

Paired-Sample t-tests		AIR FLOW RATE L/hr	
COMPOUND	MEDIA	LOW vs. MEDIUM	MEDIUM vs. HIGH
Benzene	Sand	0.76 (2.13)	0.76 (2.13)
Toluene	Sand	1.14 (2.13)	0.58 (2.13)
Ethylbenzene	Sand	0.87 (2.35)	0.13 (2.13)
Xylene	Sand	2.14 (2.91)	2.42 (2.91)
Benzene	Organic	0.29 (2.13)	0.95 (2.35)
Toluene	Organic	1.13 (2.13)	1.16 (2.13)
Xylene	Organic	1.53 (2.13)	0.34 (2.13)
Mixture of BTEX Compounds			
Benzene	Sand	0.25 (2.13)	**2.81** (2.13)
Toluene	Sand	1.92 (2.13)	**2.46** (2.13)
Ethylbenzene	Sand	0.31 (6.31)	1.81 (2.13)
Xylene	Sand	0.77 (6.31)	3.92 (6.31)
Saturated Air Used for Stripping			
Toluene	Sand	2.07 (2.13)	0.64 (2.13)

5.4.4.2 Effect of Different Conditions on Residual Contaminant Concentrations

Table 31 shows the pair-sample t-test results when comparing stripping under different conditions. In the experiments in which benzene was used a significant difference in the residual concentrations was seen at the low and medium air flow rates. When stripped from the organic soil benzene concentrations were lower than those found in the sandy soil. When comparing toluene stripped using dry air to stripping with moisture

saturated air it is clearly demonstrated that at the end of the experiments the column stripped with dry air contained low residual contaminant concentrations. A comparison of toluene stripped from a mixture to toluene stripped from a soil as an individual contaminant showed a significant difference in the residual concentrations. This finding does not fit with the pattern shown with the three other chemicals and therefore should be view with scepticism until further findings are reported that either support or refute the numbers presented here. In all other comparisons no significant variations were observed.

Table 32 - t-test Results for Comparison of Residual Concentrations Under Different Conditions

Paired-Sample t-test		AIR FLOW RATE L/hr		
CONDITION 1	CONDITION 2	LOW (≈1.5)	MEDIUM (≈ 3.0)	HIGH (≈ 6.0)
Benzene in Sandy Soil	Benzene in Organic Soil	**3.80** (2.13)	**2.36** (2.13)	2.14 (2.35)
Toluene in Sandy Soil	Toluene in Organic Soil	0.58 (2.13)	1.02 (2.13)	1.15 (2.13)
Xylene in Sandy Soil	Xylene in Organic Soil	1.96 (2.35)	1.14 (2.35)	1.74 (2.35)
Toluene in Sandy Soil using Dry Air	Toluene in Sandy Soil using Saturated Air	**3.89** (2.13)	**4.99** (2.13)	**10.04** (2.13)
Benzene Added as an Individual Component	Benzene Added as Part of a Mixture	0.78 (2.13)	0.55 (2.13)0	0.45 (2.13)
Toluene Added as an Individual Component	Toluene Added as Part of a Mixture	**2.81** (2.13)	**5.67** (2.13)	**2.89** (2.13)
Ethylbenzene as and Individual Component	Ethylbenzene Added in a Mixture	n/a	1.34 (2.13)	0.69 (2.13)
Xylene Added as an Individual Component	Xylene Added as an Individual Component	0.40 (2.35)	n/a	0.63 (2.35)

6.0 CONCLUSIONS AND RECOMMENDATIONS

Soil vapour extraction was simulated by using soil columns in the laboratory. The conditions were equivalent to those found at remedial sites which contained a dissolved NAPL contaminate plume or have been remediated to a point where all NAPL had already been extracted. Both the rate of contaminant removal and the residual chemical concentrations in the soils were determined and the following conclusions were drawn regarding the rate of contaminant removal:

1. An increase in air flow rate in columns containing sandy soil resulted in increased removal rates.
2. The air flow rates used in this study had no significant effect on the removal rate in an organic soil which had both high porosity and moisture content.
3. When moisture-saturated air was used to strip toluene from a sandy soil the recovery rates were approximately 50% of those observed when dry air was used. At the end of 100 hours in the experiment using saturated air significant mass transfer was still occurring.
4. When a mixture of BTEX compounds was added to sandy soil, the mass flow rates were lower than obtained when contaminants were stripped individually. Significant mass transfer was still occurring from the mixed contaminants at the end of the experiment.

5. Compounds with higher vapour pressures were stripped faster and were present at lower residual concentrations when stripped under similar conditions.

The following conclusions were found when examining the residual concentrations found in the soil columns at the end of the experiments:

1. When benzene and toluene were stripped from a mixture lower residual concentrations were found in the soils when the air flow rate was increased from the medium rate to the high rate.
2. The residual benzene concentrations in the organics soil were lower than those found in the sandy soil when each was stripped at the low and medium air flow rates.
3. In the experiments on toluene in the sandy soil, lower residual concentrations were found when dry air was used as opposed to saturated air. This was trend was seen at all air flow rates.

The ultimate goal of remediating a contaminated site, using soil vapour extraction, is normally to meet legislated guidelines. The residual concentrations and distributions, in each soil column, were determined and compared to the "Proposed Guidelines for the Clean-up of Contaminated Sites in Ontario" of the Ministry of Environment and Energy. The following observations were made:

1. Remediation of the two soils, with any combination of the four chemicals, to achieve the guideline background levels appears to be unlikely. The lowest residual concentrations recorded were two orders of magnitude higher than the guideline values.

2. Guideline values for industrial sites were met for some samples taken from virtually all columns, indicating that these values can readily attained under most conditions using soil vapour extraction.

3. The potable water standards for benzene are the most stringent and were met in the organic soil but not in the sandy soil. However, with increased stripping time most of the soils would likely meet the standards.

A significant amount of time was spent in developing an appropriate experimental procedure during this study. Using the method outlined in this thesis, along with the following the recommendations will be helpful in conducting similar research.

1. Reduce the moisture levels below field capacity, by applying a vacuum when draining experimental columns. This will reduce the collection of moisture at the bottom of the columns and will provide a more realistic moisture distribution, once flow is initiated.

2. Design a column from which air samples can be taken, at various heights, during the course of experiments for better understanding of the extraction process as stripping progresses.

3. Soil obtained from a site that exhibited subsurface geology typical of a site where underground storage tanks might be installed could be used in further experiments. This would enable better comparisons between laboratory work and data obtained in field studies.

4. The use of five unique flow rate, instead of three, would increase the reliability of the data obtained.

5. A lower temperature could be used that corresponded to the normal subsurface temperature. This would ensure that the laboratory conditions closely resembled the field conditions.

6. A redesign of the experimental apparatus might result in a better system to seal the columns.

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APPENDIX A: EXPERIMENTAL DATA

The data gathered during this project has been included in on the disk accompanying this thesis. All files are Microsoft Excel 5.0 spreadsheets.

Table 33 - Files Located on Disk

DATA FILE NAMES		AIR FLOW RATE L/hr		
COMPOUND	MEDIA	LOW (Apr. 1.5)	MEDIUM (Apr. 3.0)	HIGH (Apr. 6.0)
Benzene	Sand	sep16a.xls	sep16c.xls	sep16b.xls
Toluene	Sand	nov4a.xls	nov4c.xls	nov4b.xls
Ethylbenzene	Sand	oct28a.xls	oct28c.xls	oct28b.xls
Xylene	Sand	oct21a.xls	oct21c.xls	oct21b.xls
Benzene	Organic	nov11a.xls	nov11c.xls	nov11b.xls
Toluene	Organic	aug26a.xls	aug26c.xls	aug26b.xls
Xylene	Organic	sep3a.xls	sep3c.xls	sep3b.xls
Mixture of all BTEX Compounds				
Benzene	Sand	sep23a_b.xls	sep23c_b.xls	sep23b_b.xls
Toluene	Sand	sep23a_t.xls	sep23c_t.xls	sep23b_t.xls
Ethylbenzene	Sand	sep23a_e.xls	sep23c_e.xls	sep23b_e.xls
Xylene	Sand	sep23a_x.xls	sep23c_x.xls	sep23b_x.xls
Saturated Air Used for Stripping				
Toluene	Sand	oct7a.xls	oct7c.xls	oct7b.xls

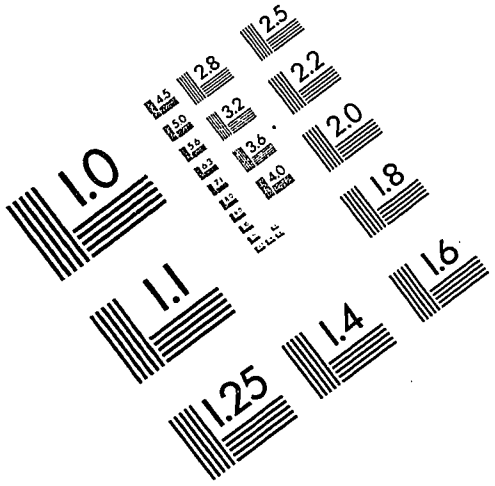
VITA AUCTORIS

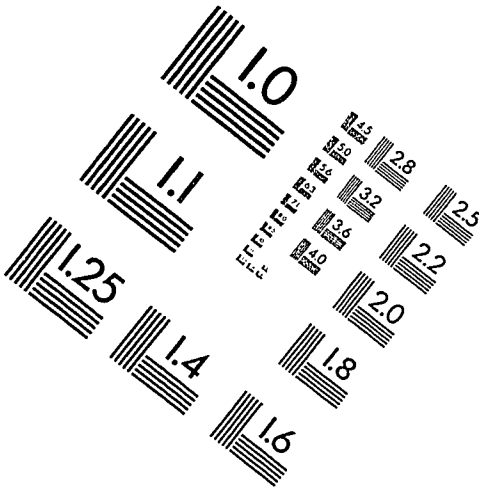
Grant Hilbers was born in Windsor, Ontario on February 1, 1972. He graduated from Brennan High School in 1990. Following High School, he attended the University of Windsor, obtaining a B.A.Sc. in Environmental Engineering in 1994. Currently he is a candidate for the Master's degree in Environmental Engineering at the University of Windsor.

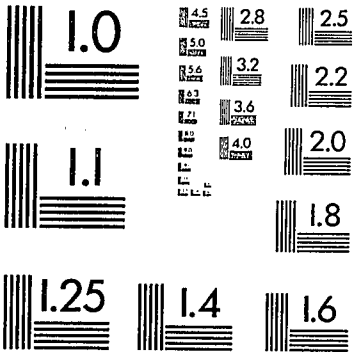
NOTE TO USERS

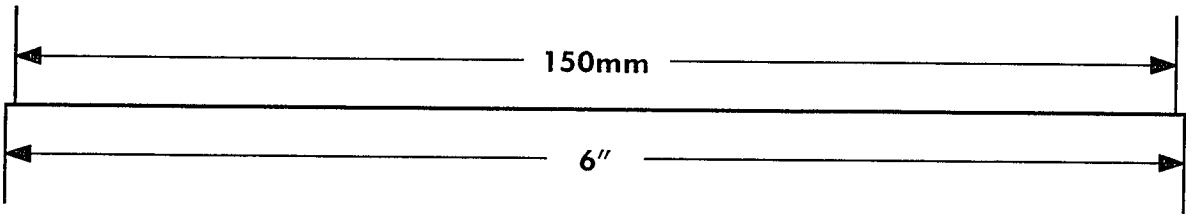
The diskette is not included in this original manuscript. It is available for consultation at the author's graduate school library.

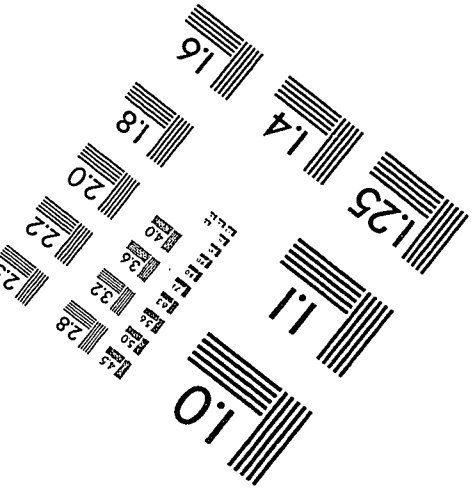
IMAGE EVALUATION TEST TARGET (QA-3)

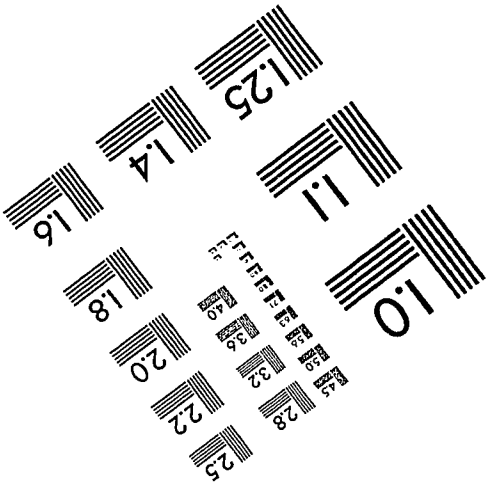












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